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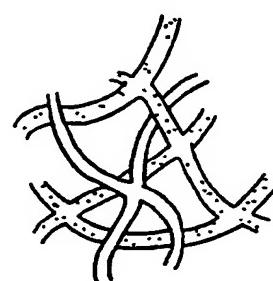
(57) Abstract

A family of composites are characterized as a network of a first fiber and at least a second fiber, where at least the first fibers have a multiplicity of bonded junctions at their point of crossing. The largest class has metals as one or both of the fibers, although the second fiber can be of materials such as carbon, ceramics, and high surface area materials. The composites can be simply prepared and manifest enormous variation in such properties as void volume, pore size, and electrical properties generally.

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MIXED FIBER COMPOSITE STRUCTURES: METHOD OF PREPARATION,

ARTICLES THEREFROM, AND USES THEREFOR

This application relates to novel composites capable of manifesting enormous variation in such properties as surface area, porosity, void volume, and conductivity, while displaying chemical stability in corrosive environments. The composites have mechanical and structural integrity and can be prepared in virtually an endless variety of shapes. For the sake of simplicity and clarity of exposition, the composites which are our invention will be discussed in this section largely from the aspect of their use as electrode materials. It needs to be stressed here that the claimed composites have significant utility outside the field of electrochemistry as will be later discussed in some detail. However, for the purpose of introducing the reader to our invention it appears better to first discuss a narrow but specific aspect prior to outlining its significantly broader features.

Carbon based electrodes are currently used in many high energy density and/or high power density applications, such as $Li/SOCl_2$ batteries, liquid double layer capacitors, and fuel cells. The maximum energy and power densities obtainable from these devices depend upon various physicochemical rate phenomena occurring at the electrode-electrolyte interface. For example, in the case of high energy density lithium/thionyl chloride batteries, deacti-vation of the carbon cathode limits operation of the battery at high (>10 mA/cm^2) discharge rates. Since deactivation arises from the preferential precipitation of solid reaction products at

-2-

the exterior of the cathode, thereby blocking its interior from participating in the reaction, the power density of the battery during discharge is limited by the porosity, the void volume, and the active or accessible surface area of the carbon cathode.

As previously stated, the low solubility of cell reaction products at the cathode severely limits operation at high discharge rates when precipitates form at the exterior surface of the cathode, blocking its interior surface area from hosting products of the cell reaction. When the cathode becomes blocked, the interfacial electrochemical reaction of the anode becomes limited by the dissolution rate of the reaction products into the electrolyte, which in turn is controlled by the precipitation rate at the cathode. Attempts to improve the fabrication and design of the carbon cathode has had limited success. Much of this activity has involved the addition of metallic elements such as copper to the carbon or the coating of the cathodes with transition metal phthalocyanines. Other efforts have utilized various carbon pretreatment procedures or different types of carbon blacks with various physical properties. However, past attempts appear not to address the intrinsic problem associated with carbon blacks, viz., the inaccessibility of small pores within the microstructure of the material and the existence of low void volumes in the outermost layers of the carbon. To provide high power density cathodes materials are needed which are flexible, have high specific surface areas, have varying and adjustable porosities and void volumes to accommodate reaction products as precipitates without significant loss of surface area, and which are corrosion resistant.

-3-

In liquid double layer capacitors the energy density increases with increased active surface area of the electrode presented to the electrolyte. On the other hand, the power density is controlled and limited by slow diffusion of electrolyte through the microporous electrode material. The combined energy and power density of these capacitors is the resultant of increased diffusion processes, which prefer large pores and high void volumes, and higher levels of specific surface area, which require small pore sizes and low void volumes. To date the requirements of large pores/high void volume and high surface area tend to be mutually exclusive. Consequently, since increased energy density involves increased surface area and increased porosity, power dense devices become more and more limited by diffusion processes as the surface area of the electrode is increased.

In fuel cells, an effective electrode material should exhibit high catalytic activity and high electrical conductivity to minimize joule losses within the device. The electrode should be highly porous to provide free access to both the gases and the electrolytes. The optimum pore size distribution of the electrode material is a compromise between several factors. For high strength, low porosity and small pores are desirable. For low polarization, large pores with maximum internal surface area are more desirable. Electrodes also contain metals such as platinum, nickel, and so forth, which are good catalysts for fuel oxidation and oxidant reduction. The catalytic activity depends on the active surface area of electrode as well as the contacting of the electrode with reactants consisting of fuel and elec-

-4-

trolyte. For this reason, controlled wetting of the electrode poses one of the more severe design limitations confronting the device in order to provide optimal contacting at the gas-liquid-catalyst interface in the absence of weeping, bubbling, and flooding.

Carbon is an especially attractive electrode material, and high surface area carbon electrodes typically are fabricated with carbon black. However, a major difficulty in fabricating and utilizing high surface area carbon electrodes has been in physically supporting the carbon. Carbon black usually is used in the powdered form which cannot be easily supported unless poly(tetrafluoroethylene) or other types of binders are used. Our radically different approach has been to combine dissimilar and normally incompatible materials to form a physically stable composite structure which exhibits properties intermediate to the constituent materials. In the context of carbon electrodes, the resulting materials have a high surface area, variable porosity and variable void volume, are structurally stable, and can be fabricated in a virtually endless variety of shapes and sizes. More particularly, high surface area carbon fibers and highly conductive metal fibers have been combined in an interwoven sinter-locked network or grid which is structurally stable. The resultant high surface area and conductive composite allows high accessibility to gases and electrolytes while providing adjustable porosities and void volumes. Interlocked networks of thin fibers can be bonded to metallic backings to provide flexible electrode structures which can be readily assembled into devices even when one of the components is relatively brittle or

does not normally bond or adhere to the metal backing.

However useful and significant the fiber network of the foregoing paragraph may be, it seemed to us that it was but one example of a class of composites with a range of uses transcending those of electrochemical applications and encompassing such diverse areas as cellular supports in biochemical reactors, magnetic separators, and filters; a detailed exposition of these and other uses is deferred to a later section. As to the composites themselves, it appeared to us that one could specify their lowest common denominator, that is, those irreducible features which are necessary and sufficient to impart to the class of our composites those characteristics which made the class desirable from a materials point of view. A necessary feature is that the composite be a network of at least two different fibers. The fibers could be chemically different, for example, a metal fiber and a carbon fiber, or they could be physically different, for example, two fibers of the same metal but with different cross-sectional dimensions. The second and only other necessary feature is that there be a number of points in the network where the fibers are physically connected, i.e., bonded. There is versatility and variability here, too, such as the relative number of bonded points, whether fibers "interbond" (i.e., bonding between dissimilar fibers), whether they only "intrabond" (i.e., bonding between similar fibers), and if there is intrabonding whether all classes of fibers so bond or whether only, say, one kind of fiber bonds.

A pictorial, somewhat fanciful, and certainly non-literal overview of our invention is depicted in Figure 1. The left hand

region, designated by A, represents a physical mixture of two kinds of fibers as shown by the open and dotted strands. The case where only one of these fibers is intrabonded is depicted by B, that where both kinds of fibers are intrabonded is depicted by C, and that where the fibers are interbonded is depicted by D. The relative amounts of the two fibers will quite obviously influence the void volume of the composite. The density of bonded points will affect structural flexibility and, where the bonded fibers are electrically conducting material, the conductivity of the composite. Where one fiber is non-porous, the relative number of the two fibers will determine the porosity of the composite. In short, from this oversimplified pictorial representation one can easily see how the final properties of the composite can be varied and one can appreciate that the properties of the composite can be a blend of the properties of dissimilar, normally incompatible materials – that is, the properties of the composite are themselves a composite of the properties of the materials forming the network. This attribute can not be stressed too highly since it is, if not unique, rarely found, difficult to achieve, and highly desirable for new materials.

The purpose of our invention is to provide as new materials composites formed from dissimilar fibers whose physicochemical characteristics may be the resultant of the physicochemical characteristics of the dissimilar fibers present, whose physicochemical characteristics can be varied, and whose properties are under the control of the fabricator. An embodiment is an article comprising a network of a first fiber

and at least one second fiber, where at least the first fiber
has a plurality of bonded junctions at the first fiber crossing
point. In a more specific embodiment each of the differing
fibers is a metal. In another specific embodiment the first
fiber is a metal and the second fiber has a surface area
between 1.5 and about 1500 m^2/g. Yet another aspect of our
invention is a method of making said composites. Other
purposes and embodiments will be apparent from the description
which follows.

Figure 1 shows how resistivity changes with surface area for
various materials.

Figure 2 depicts the assembly of paper preforms into electrode
preforms prior to sintering.

Figure 3 is a photomicrograph of a stainless steel-cellulose
composite paper before sintering, where the stainless steel
fibers are 2 microns in diameter.

Figure 4 is a photomicrograph of a stainless steel-carbon-
cellulose composite paper before sintering; stainless steel
fibers are 2 microns in diameter.

Figure 5 is a photomicrograph of the stainless steel-carbon
composite matrix after sintering the composite paper of Figure 4
at conditions of Experiment E in Table I.

Figure 6 is a photomicrograph of the stainless steel-carbon
composite of Figure 5 at higher magnification showing intimate
contacting of metal and carbon fiber after sintering.

Figure 7 is a photomicrograph at still higher magnification of
a metal-metal joint after sintering.

Figure 8 is a pictorial and non-literal overview of the

-8-

invention.

Figures 9 and 10 are electron photomicrographs at different magnifications of a composite of two different diameter stainless steel fibers; see Example 1.

Figure 11 is an electron photomicrograph of a metal fiber composite entrapping fibers of 95% alumina-5% silica; see Example 2.

Figure 12 is an electron photomicrograph of a metal fiber composite with an entrapped mica platelet and kaolinite particles chemically attached to the stainless steel fibers; see Example 3. Figure 13 is the same sample at higher magnification

Figure 14 is an electron photomicrograph of a composite of metal fibers with two different diameters having entrapped within the network a biosupport. Figure 15 is an electron photomicrograph of the same composite which has been impregnated with growing cells; see Example 4.

Figure 16 is an electron photomicrograph of a composite of stainless steel and carbon fibers; see Example 5.

Figure 17 is an electron photomicrograph of a composite of stainless steel and carbon fibers; see Example 6.

In Figure 16 the metal fibers have a diameter of two microns, a lenght of five millimeters; in Figure 17 the metal fibers have a diameter of 0.5 microns and a length of 0.1 millimeter.

Figure 18 shows polarization cureves for the reduction of oxygen in an alkaline fuel cell; see Example 7.

In the sphere of electrodes it often is desired that materials have a high surface area, high void volume, and high electrical conductivity. Although it is not necessary that all three

attributes be manifested simultaneously in every physical device
utilizing an electrode, it would be quite desirable to have an
electrode material which not only permits variability in these
properties, but also affords the option of preparing an electrode
with that set of properties optimum for a particular application.
Properties such as high surface area and high electrical
conductivity tend to be mutually exclusive, as is illustrated in
Figure 1. This situation arises because, for example, carbon has
a low density (relatively high surface area) and modest
conductivity whereas metals have a high density (relatively low
surface area) accompanied by a generally high conductivity.
Consequently, the properties of prior art materials, and in
particular the mutual exclusivity of two of the three properties
given above, restrict the set of simultaneously attainable
properties available and preclude the option of complete design
manipulation.

Conceptually a marriage of carbon and metals might result in a
composite with the best features of both. However, carbon blacks
and metals do not form strongly adhesive bonding arrangements
with each other and possess quite different densities and tensile
properties. Consequently they do not mix well when dry nor
provide good adherence to metal substrates under normal
conditions. As previously stated, our goal has been to combine
dissimilar and normally incompatible materials to form a
physically stable composite structure which exhibits properties
that are intermediate to the constituent material. This goal has
been achieved successfully in the inventions which are described
within. One embodiment is a composite which is a matrix of car-

bon fibers interwoven or interlocked in a network of fused metal fibers. Another embodiment is an electrode of the aforementioned composite bonded to electrically conducting material. Yet another embodiment is a preform for the composite comprising a dispersion of carbon fibers, metal fibers, and an organic binder where at least 99% of the latter is converted to volatile materials under conditions sufficient to fuse the metal fibers with a loss of less than 15 weight percent carbon. Yet another embodiment is a method of making the composite comprising preparing a uniform dispersion of carbon fibers, metal fibers, and solid cellulosic binder in a liquid medium, collecting the wetted uniform solid dispersion and removing the liquid medium from it to afford a preform, heating the preform in a gaseous atmosphere at conditions sufficient to vaporize at least 99% of the binder and to fuse metal fibers with a weight loss of less than 15% of carbon fibers, and recovering the resulting composite.

As stated above, the composite of this invention is a matrix of carbon fibers interlocked in and interwoven among a network of fused metal fibers. Although it should be apparent that "carbon" in the phrase "carbon fibers" includes and encompasses graphite, we here specifically note that in the context of the remainder of this specification and in the claims "carbon fibers" includes graphitic material. The carbon fibers constitute from about 1 to about 98 weight percent of the final composite, although the range between about 20 to about 98 weight percent is preferred. There is no significant upper or lower limit for the diameter of the carbon fibers as regards the composite itself. That is, the

diameter of the carbon fibers used in the composite influences its final properties rather than imposing limitations on the composite itself. Carbon fibers have been reported with a surface area from about 1500 m^2/g to 1 m^2/g and less, and with a diameter from 20 nm to about 1 mm. As an example, and as will become clearer from the descriptions within, for use in liquid double layer capacitors, $H_2/H_3PO_4/O_2$ fuel cells, and $Li/SoCl_2$ batteries, carbon fibers having a surface area of from 250 m^2/g to about 1000 m^2/g is most desirable with fibers having a diameter from 1 to about 10 microns, with a carbon content of the composite ranging from 30 to about 90 weight percent.

The carbon fibers generally are present as bundles. Single fibers tend to be brittle, whereas bundles or aggregates of fibers afford a composite with more desirable mechanical properties. As the diameter of the carbon bundles increases, the weight of metal fibers needed to keep the bundles interwoven or interlocked is decreased. The physical properties of the final composite also depend on the physical properties of the carbon fibers used; thermal stability, surface area, mean pore diameter, mechanical flexibility, resistance to electrolytes and acids, and electrocatalytic properties are examples of composite properties which are influenced by the properties of the constituent carbon fibers and any electroactive materials impregnated on the fibers. It should be emphasized that the surface area of the carbon fibers used largely determines the surface area of the final composite. Since different applications require different characteristics, the choice of carbon fiber properties often will be dictated by composite application. For example, where used in

.double layer capacitors one generally wants a certain minimum pore size, which in turn limits the surface area. In batteries mass transfer is more important and one wants a higher void volume, preferably with a bimodal pore size distribution. A graded porosity also is possible to attain using this invention and may be important in particular applications. However, what needs to be emphasized is that many of the composite properties are not only variable but are under the control of the investigator or fabricator within quite broad and flexible limits.

The carbon fibers are interwoven among, and interlocked in, a network of metal fibers. The metal fibers which may be used in the practice of this invention must be electrically conducting when used in an electrode, must be chemically inert under the conditions of their contemplated use, and must provide structural integrity and mechanical stability to the final composite under the contemplated conditions of use. So, for example, the final composite generally needs to retain its overall shape, and to retain the carbon fibers in the network relatively rigid and immobile. Examples of metal fibers which may be used in the practice of this invention include aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, beryllium, iridium, silicon, and combinations of the above. Metal alloys also may be used in the practice of this invention, as exemplified by constantan, hastelloy, nichrome, inconel, monel, carpenter's metal, and

various steels, especially stainless steels, and other iron alloys. As can be appreciated, there is enormous flexibility in the choice of metal fibers. Because of their general availability and relatively modest cost, as well as favorable physical and chemical properties, various stainless steels are the materials of choice, especially in many electrode applications.

The diameter of the metal fibers used is largely dictated by their availability. Although in principle there is no upper or lower limit to metal fiber diameter there may be significant operational restrictions. For example, if the metal fiber diameter is greater than ten times, or less than one-tenth, the carbon fiber diameter, then the fused metal network may not hold the carbon fibers together adequately. Stated differently, the metal fiber diameter D_m relative to the carbon fiber diameter D_c is in the range $0.1D_m \leq D_c \leq 10D_m$. Another operational limitation is related to the number of metal-metal contacts, or fusion points, which are largely responsible for supporting the carbon fibers in the composite. Calculations show that the number of metal-metal contacts varies inversely with the square of the metal fiber diameter, hence there is a requirement for small diameter metal fibers where it is desirable to increase the overall weight fraction of carbon and surface area of the resulting composite. But in the context of novel composites per se, the diameter of the metal fiber used is not critical. The method of preparation and attainment of composites is not limited by metal fiber diameter, at least up to about 50 microns. In the context of composite properties, however, the diameter of the metal fiber

-14-

is important. In practice it is desirable to have metal fibers with a diameter under about 10 microns. It would be most desirable to use metal fibers with a diameter in the range from about 0.5 microns to about 4 microns, but it needs to be emphasized again that the nature and diameter of the metal fibers used in the practice of this invention are limited largely by their availability rather than by any theoretical considerations.

The amount of metal in the final composite depends on how much surface area per gram is important, and, perhaps even more importantly, how good a contact is desired between the metal and the carbon fibers. It should be clear that the better the contact wanted, the higher the necessary percentage of metal fiber (at constant fiber diameter) in the final composite. Generally the composites of this invention will have a metal content ranging from about 2 up to about 99 weight percent. As metal content increases, the composite shows reduced resistance and higher power density per gram with a lower surface area and lower energy density per gram.

The carbon and metal fibers are mixed with a binder to afford a preform, which is a solid containing a non-woven dispersion of the fibers. The binder provides a matrix in which the fibers of the carbon and metal are dispersed. The purpose of the binder is to permit the fabrication of a solid preform containing an otherwise structurally unstable dispersion of the elements of the final composite, - i.e., carbon and metal fibers - which can be shaped, stored, and otherwise handled prior to creation of an interlocked network via fusion of the metal fibers. The binder merely provides a stable, although weak, physical structure which

-15-

maintains the spatial relationship of the components of the final composite prior to the latter's formation. Although the preform is only a temporary structure, it is an important one in the fabrication of the final composite. The binders used in preparation of the preform also may contain adjuncts, such as pore and void formers.

One critical property of the binders which may be used in the practice of this invention is that they volatilize at least to the extent of 90 weight percent, and preferably at least 99 weight percent, under conditions used for fusion of the metal fibers. The binder has no function in the composite, hence its presence should be minimal. Among binders which may be used in the practice of this invention are cellulose, organic resins such as polyvinyl alcohols, polyurethanes, and styrene-butadiene latex, and thermosets such as epoxies, urea-formaldehyde resin, melamine-formaldehyde resin, and polyamide-polyamine epichlorohydrin resin. Cellulose appears to be the premier binder because it volatilizes completely at relatively low temperatures with little ash formation and is unreactive toward the other components of the composite.

The binder is present in the preform at a range from about 2 up to about 80 weight percent. The minimum amount of binder is that which is necessary to give a stable preform, that is, one which can be handled, shaped, and so forth, an amount which depends upon carbon fiber loading, fiber size, and so forth. The amount of binder present in the preform will influence the void volume of the final composite, with a higher binder content affording a higher void volume, hence the binder can be used as one

-16-

independent variable to control this property. Using cellulose with carbon fibers and stainless steel fibers as an example, a range from about 10 to about 60 weight percent of cellulose is a typical one.

The carbon and metal fibers are mixed with the binder and with a liquid of appropriate viscosity. The purpose of the liquid is to provide a medium for the facile and effective dispersion of the solids, for one wants as uniform a dispersion as is feasible in the final preform. Other than the need for the liquid being unreactive with the components, there are no other important limitations on the liquid which may be used. In the case of cellulose water normally will be the liquid, although water-alcohol mixtures, especially water-glycol, may be used. Illustrative examples include methanol, ethanol, propanol, ethylene glycol, propylene glycol, butylene glycol, poly(ethylene glycol)s, poly(propylene glycol)s, and so forth. The liquid medium also may contain salts where desirable.

After a dispersion is attained, the solids are collected, as on a mat. Excess liquid may be removed, such as by pressing, and the resulting solid dispersion is then dried. Where a thermosetting binder is used the temperature of drying is important. However, in the more usual case there is nothing particularly critical in the drying process, and drying may be performed in air, under elevated temperatures, or in a flowing gas. The mass also may be compacted to a greater or lesser extent to affect void volume; the greater the compaction, the lower will be the void volume.

Fusion or sintering of the metal fibers in the dried preform,

-17-

whose preparation was described above, is the final stage in the fabrication of the composite. The preform is heated under conditions effecting sintering of the metals to provide a network of fused metal fibers. Fusion of the metal fibers at their points of contact rigidly locks the carbon fibers in place to afford a rigid structure by defining a matrix of carbon fibers interwoven or interlocked in a network of metal fibers with the structural rigidity arising from a multiplicity of fused points of contact. Sintering typically is done in a gas containing hydrogen at a partial pressure which is about 5 times the partial pressure of water in the gas stream, the water typically arising from the binder and from oxides on the surface of the metal. At the temperature of metal fusion the metal also usually promotes gasification of carbon via its reaction with hydrogen to afford methane. Consequently sintering preferably is performed at a high temperature for a short time to promote metal fusion relative to carbon gasification. It is desired that sintering be accompanied by loss of less than about 25% by weight of the carbon fibers via gasification, preferably under about 15%, and even more preferably under about 5 weight percent loss. Although the nature of the materials in the preform are important to determine the particular fusion conditions, the relative amounts of these materials are less important. The optimum sintering temperature can be routinely determined by the skilled worker in this field through simple experimentation. For example, where a carbon fiber-stainless steel composite is obtained through a preform with cellulose as a binder it has been determined that fusion temperatures from about 1000°C to about 1200°C for a

period from 2.5 minutes to 3 hours is optimum in an atmosphere of H_2 at 101 KPa. It may be noted in passing that controlled void formation is a consequence of binder volatilization.

It needs to be appreciated that although the foregoing temperatures provide a workable range, the properties and composition depend on the sintering time and temperature. Sintering at 1200°C for 5 minutes produces an electrode material very different than one formed using the same preform and sintering at 1000°C for 3 hours. Depending on the specific application, either one might be considered optimal. Certainly the corrosion resistance of the metal and the metal/carbon ratio are greatly affected by the sintering conditions shown. The polarization resistance also depends on the conditions.

As stated at the outset, the properties of the composite may be varied over rather wide ranges. The surface area of the composite depends upon the amount of carbon present as well as the surface area of the carbon fibers used in its preparation. It is desirable to have a composite with a high surface area where the composite is used as an electrode, but with a low surface area where the composite is used for electromagnetic shielding. The surface area of the final composite may range from about 0.001 m^2/g to at least 1350 m^2/g. In the general field of electrochemistry, the most interesting range of surface areas is from about 50 to about 1350 m^2/g, especially the range 250-1000 m^2/g. The void volume of the composite determines its ability, when used as an electrode, to accommodate solid precipitates without affecting electrode surface area, and the ability to provide good heat and mass transfer. Void volume, as

-19-

mentioned above, may be adjusted by the amount of the binder used, as well as the diameter of the binder fibers and the application of pressure during sintering. Clearly this is under the control of the investigator who then has the capability of fabricating composites with that set of properties desired for a specific application.

In the case of bipolar electrodes, required for liquid double layer capacitors, $Li/SOCl_2$ cathodes and $H_2/H_3PO_4/O_2$ fuel cells, preform materials are placed on both sides of a thin metal foil and sintered, as described earlier, so that the metal fibers lock the high surface area carbon fibers to both sides of the electrode foil. The metal foil serves as an electrolyte barrier and an electrode base for connecting external contacts. Metal fibers and the electrode base may be fabricated from the same material, although dissimilar metals can be used provided highly adherent and sinter-bonded contacts can be formed.

As stated earlier, the composites of our invention have a multiplicity of diverse uses in addition to that of an electrode. For example, the composite paper preforms can be stacked and sintered with varying pore sizes, void volumes, etc., so as to form tailored filter materials. These filter materials can be wrapped around an appropriate mandrel so that near net shape properties are obtained upon sintering. There does not appear to be any major limitation on the fiber materials which are used. The independent adjustment of pore size and void volume would help to make, e.g., stainless steel filters, which provide long lifetimes and lower pressure drops prior to plugging.

Superconducting magnetic separators, with appropriate screen

-20-

materials, are routinely used in the minerals beneficiation
industry to remove magnetic ores and particulates from
nonmagnetic crudes. The force which attracts the magnetic
particulate depends upon a number of factors one of which is the
magnitude of the magnetic field gradient at the magnetic screen.
Material holdup and retention, and clogging prior to
demagnetization with shaking and rinsing also are design
criteria.

In the past, methods have not existed for making screen
materials with independent optimization of void volume, pore size
and fiber diameter. Fiber diameter is important since the radius
of the wire and holes or voids in the resultant mesh control the
magnetic field gradient. Currently, 400 grade stainless steels
with appropriate magnetic properties are employed in these
screens, but fibers below 10 or 20 μm are generally not used
since the screen or mesh which is formed plugs easily due to the
formation of small voids and/or becomes weak when small diameter
materials are employed if the voids are kept large (viz., low
density materials).

Our process (i) is directly applicable to 400-grade stainless
steels, (ii) can be used to achieve relatively independent
control of void volume and pore volume, (iii) can fuse small
diameter loose fibers into networks that are not available as
free-standing starting materials, (iv) can be used to form
layered/stacked sheets for graded porosities and enhanced
performance and (v) can utilize mixtures of both large and small
diameter fibers. The latter approach would permit larger fibers
to be used for structural support while high gradient zones could

be affixed to these members using smaller diameter materials.
Indeed, the possibilities here seem endless.

In the case of bipolar electrodes, required for liquid double
layer capacitors, $Li/SOCl_2$ cathodes, and $H_2/H_3PO_4/O_2$ fuel cells,
preform materials are placed on both sides of a thin metal foil
and sintered, as described earlier, so that the metal fibers lock
the high surface area carbon fibers to both sides of the
electrode foil. The metal foil serves as an electrolyte barrier
and an electrode base for connecting external contacts. Metal
fibers and the electrode base may be fabricated from the same
material, although dissimilar metals can be used provided highly
adherent and sinter-bonded contacts can be formed.

The experimental description and results which follow only
illustrate this invention and are representative of the methods
which may be used and the results which may be obtained, but
should not be considered as limiting the invention in any way.

Materials--The constituent materials employed during electrode
preparation were carbon fibers from Charcoal Cloth, Ltd., 316L
stainless steel fibers from Bekaert Steel Wire Corp., cellulose
fibers as a mixture of soft and hard woods, and 316L stainless
steel foils from Arnold Engineering. Individual carbon fibers
were 2-3 microns in diameter but were used in the form of 20
micron diameter bundles up to 5 mm in length containing ca. 30
individual fibers. Stainless steel fibers were 2 microns in dia-
meter and 2 mm in length. Cellulose fibers were 20-30 microns in
diameter and varied in length from 100 to 500 microns. The
stainless steel foils were 5 microns in thickness.

Fiber preparation--Before the various fiber materials could be

-22-

combined into a paper preform, the carbon and stainless steel fibers required separation and dispersion into a slurry for easy mixing with other materials. In raw form, the carbon fibers were bundled and twisted into strands and woven into charcoal cloth. The "cloth" was dismantled into strands, then cut into 0.5 cm sections to allow for dispersion of individual fiber bundles in water. "As received" stainless steel fibers were coated with polyvinyl alcohol (PVA) type Mowiol 4-88, which was utilized during sizing and cutting prior to shipment. PVA was removed by repeated rinsing of these fibers in distilled water.

Formation of paper preform--Since physical mixtures of metals and carbon fibers are not mechanically stable, cellulose fibers were employed as a binder to form paper preforms. The paper preforms used in electrode preparation were processed according to TAPPI Standard 205 using Noran equipment. The pretreated carbon and stainless steel fibers along with cellulose fibers were agitated at 50 Hz in 1 liter of water for five to twenty minutes. The dispersed fiber mixture was then collected on a sheet mold (200 cm^2) to form the wet paper composite preform. The preform was pressed at ca. 400 kN/m^2 and allowed to dry in air at room temperature.

Assembly of electrode preforms--The carbon-stainless steel-cellulose composite papers (i.e., paper preforms) and stainless steel foils were cut into circular disks with diameters of 13 and 19 mm respectively, and assembled by layer as shown in Figure 2. In most cases, an optional 19 mm diameter sheet of stainless steel-cellulose paper preform was placed on top of each side of the composite structure to serve as a protective layer as shown

in Figure 2.

The composition of the composite paper preforms used in electrode fabrication and composite preparation whose results are reported below was 50% carbon (1.0 gm), 25% stainless steel (0.5 gm), and 25% cellulose (0.5 gm). The protective overlayer consisted of 50% stainless steel (0.5 gm) and 50% cellulose (0.5 gm).

Sintering of electrode preforms--The layered electrode preform shown in Figure 1 was placed between two quartz plates (20 x 30 mm), which were held in place by a quartz clip. The sample was placed in a controlled atmosphere quartz U-tube reactor (25 mm diameter) for heat treatment. The sintering reactor was equipped with flexible gas lines to facilitate movement of the reactor into and out of the vertical sintering furnace (Heviduty, 10 A, 1150 W). Sintering was performed in a reducing atmosphere of H_2 with a flow rate of 10-100 cc/min (STP) and total pressure of 101 kPa. Gases were supplied by Liquid Air with purities of 99.995% for H_2. Gas flow was monitored using a Linde Model FM-4550 flow controller.

The feed gas mixture was passed over Cu turnings at ca. 500 K to remove background CO, CO_2, O_2 and H_2O and then passed through a molecular sieve trap immersed in a liquid N_2 trap to further remove background condensibles. The sintering reactor was passivated with feed gas for a minimum of three hours prior to reaction. The sintering furnace was preheated to 1423 K prior to beginning each experiment. The reactor was then introduced into the furnace causing a rapid cooling of the furnace to ca. 1400 K. The experimental temperature was typically reached in 5-7 min

-24-

followed by sintering at the desired temperature. The sintering

reactor was quenched by rapidly removing it from the furnace.

Sample analysis--The amount of carbon retained in the electrode

after sintering was estimated from weight change measurements.

These measurements were obtained on a Sartorius Model R 160 D

semimicro balance with a precision of 0.02 mg.

Volumetric N_2 B.E.T. surface area measurements were performed

to determine whether the high surface area characteristics of the

carbon had been retained.   Measurements were taken of virgin

charcoal cloth before paper preform preparation and of composite

electrodes after sintering.   The B.E.T. apparatus employed was a

high-vacuum Pyrex design with a base pressure of $4*10^{-2}$ Pa.   To

minimize background impurities, high-vacuum greaseless stopcocks

(Ace Glass) were used to manipulate gas storage and dosage.

Experimental pressures were monitored within 1.3 Pa using a Texas

Instruments precision manometer (Model 145) employing a fused-

quartz Bourdon capsule.   Samples were pretreated by heating in

vacuum at 473 K for a minimum of 2 hrs to remove species such as

water from the sample.   For each experiment performed, a minimum

of four data points were collected over the pressure range of 5.1

to 30 kPa.

The surface compositions of stainless steel foils in the

sintered composite were determined using X-ray photoelectron

spectroscopy (XPS).   XPS analysis was performed using a Leybold-

Heraeus LHS-10 spectrometer utilizing MgKα X-rays.   The sample

was exposed to air for ca. 100 hours before measurements were

performed, allowing the surface to oxidize.   Analysis was

performed at 300 K under a vacuum of $1.3*10^{-6}$ Pa. Surface

-25-

compositions were calculated on the basis of measured peak area ratios normalized with respect to the appropriate cross sections, inelastic electron escape depths, and spectrometer sensitivity factors.

Scanning electron microscopy (SEM) was utilized to observe the degree of intermixing of the constituent fibers and sintering behavior. SEM micrographs were collected on an ISI Model 5540 scanning electron microscope at 5 kV beam energy.

Table I shows carbon retention and sintering resuls for several sintering conditions.

Retention of carbon--The amount of carbon retained in the sintered composite matrix was determined by weight change measurements with the assumption that the metal weight would not change during sintering and that all cellulose would be converted to gaseous products. Separate experiments verified that the weight of retained cellulose after exposure to hydrogen at 1323 K was negligible. At these conditions, the weight change of stainless steel was not detectable. Based on carbon retention measurements, "optimal sintering" determined by the percentage of initial carbon remaining in the sintered electrode, was achieved at 1423 K in H_2 for 2.5 minutes. Gas flow of the H_2 was maintained at 10 cc/min (STP) with a total pressure of 101 kPa. For these optimal sintering conditions, carbon retentions of >98% were attained. Results of selected sintering experiments are shown in Table I.

-26-

Experiment	Temperature (K)	Time (min)	Percentage of Initial Carbon Retained (%)	Degree of Sintering

Table I.   Carbon Retention as a Function of Sintering Conditions

Experiment	Temperature (K)	Time (min)	Percentage of Initial Carbon Retained (%)	Degree of Sintering
A	1323	10	97.3	G
B	1323	5	ND	NS
C	1373	5	97.5	G
D	1373	2.5	ND	NS
E	1423	2.5	98.3	G
F	1423	1.5	ND	NS

G - Good, appeared structurally stable

ND - Not Determined

NS - Not Sintered, no structural integrity

B.E.T. surface area--Of equal importance to the retention of carbon is the requirement that carbon retains its high surface area structure after sintering. Volumetric B.E.T. measurements showed a surface area of ca. 760 m^2/gm of carbon for the sintered composite electrode structure compared to ca. 790 m^2/gm for virgin charcoal cloth.

Surface composition--XPS measurements of stainless steel foils that had undergone sintering at the conditions of Experiment H in Table I showed that iron was the most abundant metallic surface species. The surface abundance of iron, chromium, and nickel were investigated. The peak shapes and locations obtained are consistent with those reported for iron (+3) oxide (Fe_2O_3) and chromium (+3) oxide (Cr_2O_3) (21). Fe_2O_3

was found to be 1.8 times more plentiful than Cr_2O_3 on the surface. No nickel oxide (NiO) was detected. Results for the bulk and surface compositions of sintered 316L stainless steel foils are presented in Table II.

Table II.   Bulk and Surface Composition of
            Stainless Steel Type 316L Foil.

	Bulk Composition (atomic %)	Surface Composition (atomic %)	Heat of Sublimation (kJ/mol)
Chromium	17	35	396
Iron	71	65	416
Nickel	12	ND	429

ND - Not Detected by XPS

Composite matrix structure--The degree of intermixing of the fibers in the composite electrode matrix was investigated using SEM. Figures 3 and 4 show micrographs of the stainless steel-cellulose and stainless steel-carbon-cellulose composite paper preforms, respectively, prior to sintering. The degree of interconnectedness of the metal and the carbon fibers in the two paper preforms is clearly shown in the micrographs.

Figure 5 shows the metal-carbon composite matrix after sintering following the conditions of Experiment E in Table I. No cellulose appears in the structure and the interwoven framework of the sintered composite is evident. The intimate contacting of stainless steel and carbon fibers can be seen in Figure 6. Figure 7 shows the degree of metal-metal sintering which occurs in the sintered matrix. This sintering appears responsible for the electrode's structural integrity and electrical conductivity.

-28-

In another, broader embodiment of the invention, we have found a generalized method of making shaped composite articles which is enormously versatile both with respect to the materials of the resulting composite as well as the shape of the resulting article. Our method bonds fibers at a plurality of their junctions in a fibrous network, which inter alia has the effect of imparting high strength and structural integrity to the fibrous network and to afford good electrical contact when one of the fibers is a metal or another type of conductive, or conductively coated, material. One result of our method is that it is possible to combine dissimilar materials with dissimilar properties where the materials and properties often are considered incompatible or mutually exclusive, and to obtain an article having mutually beneficial properties characteristic of each of the dissimilar materials.

Because of the broad operability of our method when applied to a wide spectrum of materials, we have examined the resulting articles of manufacture as to their properties, as to their several uses, and as to the variants which can be expected based on our experience. In one aspect, then, our invention is a generalized method of making shaped articles containing at least two kinds of fibers bonded in a network. In another aspect our invention is the various composites which result from the method of our invention. The lowest common denominator of these articles, that is, the feature which is common to each of them, is a network of at least two classes of fibers where the fibers from at least one of the classes are bonded at a multiplicity of junctions within the network. This theme will be elaborated upon

-29-

in greater detail below.

     We use the term "network" in the usual dictionary definition,
i.e., a structure of [cords or wires] that cross at regular
intervals and are knotted or secured at the crossing.   See
Webster's Seventh New Collegiate Dictionary, G. and C. Merriam
Co., (1970), p. 568. We note that the networks of our invention
are two dimensional in the sense that the flat-shaped article has
a thickness which is small relative to other dimensions. However,
the diameter of the largest size fiber also will be small relative
to the thickness of the article, which means that the articles of
our invention are not truly a monolayer of fibers but instead are
composed of multiple layers of discrete fibers. In the context of
the definition of a network, the crossing points of the fibers may
be in different planes, and it follows that the fibers will not be
in contact at all crossing points. In this application
"junctions" refers to the crossing points in the network where
fibers are in contact or caused to come into contact.

     As previously stated, the feature common to all articles of
our invention is a network of at least two classes of fibers where
at least one class is bonded at a plurality of their junctions.
By "bonded" is meant that the fibers are physically connected,
either directly or via a link or bridge between the fibers. In
particular, "bonded" does not include mere physical contact of two
fibers but rather requires some sort of permanent union or "gluing
together" of the fibers; bonded fibers are securely connected and
firmly attached, resisting separation. Note also that two fibers
can be bonded without their being in direct physical contact, but
with indirect contact provided by a link or bridge between them.

-30-

Whether only the first fibers are bonded at their junctions or whether both the first and the second fibers are bonded at their junctions depends on the materials of the article, the bonding method, and the bonding conditions. Similarly, the question whether the first and second fibers are bonded to each other also depends on the fibrous materials, the bonding method, and bonding conditions. For example, where both the first and second fibers are of the same metal, then generally both the first fibers will be bonded to each other at their junctions and the second fibers will be bonded to each other at their junctions, as well as the first and second fibers being bonded to each other at their junctions. Where, for example, the second fiber is a metal which is dissimilar from that of the first fiber, and where the bonding method is sintering, then the question of whether the second fiber will be bonded at its junctions will be dependent upon sintering temperature and sintering time as well as the particular metal constituting the second fiber. Similar considerations apply to the question whether the first and second fibers will be bonded at their junctions. In contrast, where the first fiber is a metal and the second fiber is, for example, a ceramic, the kind of bonding will be quite dependent upon the particular bonding method and bonding conditions. So, for example, where heating is the bonding method then at sufficiently high temperatures to sinter both the metal and the ceramic the first fiber will be bonded at its junctions and the second fiber bonded at its junctions, but generally there will be no bonding at the junctions of the metal and the ceramic.

On the other hand, where the first fiber is a metal and the

second fiber a non-metal, if electroplating is the bonding method
and if the second fiber can be electroplated under the conditions
employed, then there would be bonding at all junctions. Where
only the metal is electroplated under the conditions used then
only the junctions of the first fiber will be bonded. For
example, electrodeposition of nickel onto or into the metal fibers
in a network of 2 micron diameter stainless steel and 2 micron
diameter carbon fibers causes a physical enlargement of the metal
fiber diameters which leads to an increase in the electrical and
physical contact between carbon and metal by greater than 30%.
Such a procedure provides one example whereby bonding between
dissimilar materials can be enhanced for desired electrical
properties or other favorable mechanical attributes. In any
event, the question of what junctions are bonded generally can be
answered from a knowledge of the materials used, the bonding
method and bonding conditions employed, and, in appropriate cases,
through further simple experimentation.

Among the bonding methods which may be used in the practice
of our invention are included heat, electroplating, chemical bond
formation, chemical vapor deposition, plasma spraying,
thermosetting, dipping and drying in a solution of an organic
binder (structure forming agent; vide infra) and solvent,
application of pressure to a mixed composite fiber network which
flows, melds, creeps, etc., or any other procedure which causes
physical attachment of all, or various types of selected, fibers
within the network.

Heating may cause similar or dissimilar metals or ceramics to
sinter via the atomistic diffusion of surface atoms so as to form

-32-

solder-like joints which provide good electrical and/or mechanical contact. Alternatively, heating may cause dissimilar metals and materials to overcome diffusive or reactive energy barriers permitting surfaces of metalized or polymer-coated fibers to bond at conditions different, or significantly less severe, than those otherwise required to bond the base materials. The thermosetting properties of polymeric or noncrystalline materials may also be used to fuse these materials during an appropriate heat treatment with the simultaneous application of an applied pressure force.

Electrodeposition of a metal (electroplating) into or onto the mixed fiber composite provides a mechanism for growing or thickening and strengthening contacts which are present or formed between electrically conductive materials onto which the metal is deposited. It also provides a mechanism for increasing the electrical conductivity of the matrix, and, as noted earlier, conductor "swelling" during electrodeposition can increase the contact between conductive and nonconductive fiber materials. Alternatively, electroplating via electroless deposition from a metal salt and a suitable organic reducing agent can be used as an indiscriminate bonding procedure which is operative regardless of the base electrical conductivity of the material coated (e.g., aqueous silver nitrate plus formaldehyde produces a colloidal suspension of reduced metal which bonds via precipitation and forms adherent metallic films on various substrates).

Chemical vapor deposition and reactive plasma spraying provide well-documented means of growing thin-films and coatings which have the ability to coat, in a relatively uniform manner regardless of geometry, various articles despite their dissimilar

electrical or mechanical properties. These procedures therefore have the ability to bond similar or dissimilar materials which are in relatively close proximity. Since the embodiment of this invention many times involves mixtures of microscopic fibers in intimate contact, the growth of a secondary deposit via, e.g., chemical vapor deposition, can cause physical attachment of these materials at locations which had previously been in close proximity but not in direct physical contact. This is an example where two fibers are bonded via a bridge between them.

Dipping a composite fiber matrix in a solvated organic binder or resin can cause attachment of similar and dissimilar fibers when the solvent is removed by gradual drying and the binder is concentrated via surface tension effects at the interstices and intersections of the fibers (e.g., polyvinyl alcohol in water). Subsequent drying leads to the physical attachment of the fibers and high temperature carbonization or graphitization of the organic can be performed to make the interconnecting material electrically conductive. Alternatively, a solvated inorganic metal salt can also be deposited upon drying at the intersections of the fibers with this material being subsequently reduced to produce a conductive coating and physical attachment.

Still another method of attachment might involve an ambient temperature attachment of fibers through the application of pressure exceeding that required to cause the material to flow via plastic deformation. Such a process could be performed and/or facilitated via the addition of an organic fiber or through the use of a combined heat and pressure treatment.

In those cases where the first fiber is either a metal or a

ceramic heating can be used effectively to sinter-fuse the fibers
at their junctions. The sintering temperature and sintering times
will vary greatly depending upon the nature of the materials to be
fused as well as the nature of the second fiber, but these
generally can be determined either via simple experimentation or
through knowledge of the activation energy of the various
processes which occur during sintering. For example, in the case
where the first fiber is stainless steel and the second fiber is
carbon and the sintering is done in the presence of hydrogen, then
the competing reactions are fusion of the stainless steel and
vaporization of carbon through reaction with hydrogen, especially
if catalyzed by the metal. Experimentation has shown that the
activation energy of the latter process is substantially less than
that of the former. In addition, the latter process is dependent
on hydrogen pressure. Therefore, the selectivity of sinter fusing
the stainless steel at its junctions may be optimized by heating
under low hydrogen partial pressure at relatively high
temperatures for relatively short times.

The particular bonding method as well as the conditions of
bonding will understandably depend upon the nature of the fiber
materials in the composite as well as its intended use. For
example, where the first fiber is a metal and the composite is
intended for use as an electrode, where good electrical contact
between the metal fibers is required, it is found that bonding via
sintering is quite effective. However, it also has been found
that bonding at the junctions is further improved by
electroplating. The message we wish to convey is that however
significant may be the bonding method in the general practice of

our invention, the choice of the particular bonding method used necessarily depends upon the nature of the fibers in the composite as well as the intended use of the composite.

Perhaps the most important subclass of composites is that where the first fiber is a metal. Virtually any metal fiber may be used in the practice of our invention, although generally the metal must be chemically inert under the conditions of the contemplated use of the composite and also generally must provide structural integrity, strength, and mechanical stability to the final composite under the contemplated conditions of use. For example, the final composite generally needs to retain its overall shape and to remain relatively rigid and immobile in most uses. However, where the final composite needs to retain some flexibility in its operating environment then materials need to be chosen which will impart such properties. Examples of metal fibers which may be used in the practice of this invention include aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, berrylium, iridium, silicon, magnesium, manganese, gallium, and combinations of the above. Metal alloys also may be used in the practice of this invention, as exemplified by constantin, hastelloy, nichrome, inconel, monel, carpenter's metal, and various steels, especially stainless steels, and other alloys. As can be appreciated, there is enormous flexibility in the choice of metal fibers which adds to the attractiveness of our invention.

The diameter of the metal fibers used is largely dictated by

their availability. Although in principle there is no upper or
lower limit to metal fiber diameter, there may be operational
restrictions in those cases where the second fiber is a non-metal
which is held together by the fused metal network. For example,
if the second fiber is a carbon fiber which is interwoven among
fused metal fibers, then if the metal fiber diameter is greater
than ten times, or less than one-tenth, the carbon fiber diameter
the fused metal network may not hold the carbon fibers together
adequately. But in the more general case the ratio of diameters
of a metal first fiber to second fiber may range from as high as
1000 to as low as 0.001, depending upon the nature of the fibers,
their density, and the intended use of the article inter alia.
Another operational limitation may be related to the number of
bonded junctions which are largely responsible for supporting the
carbon fibers in the aforementioned composite. Calculations show
that the number of such junctions varies inversely with the square
of the metal fiber diameter, hence there is a requirement for
small diameter metal fibers where it is desirable to increase the
overall weight fraction of carbon of the resulting composite. But
in the context of novel composites per se, the diameter of the
metal fiber used is not critical. The method of preparation and
attainment of the composite is not limited by metal fiber
diameter, at least up to about 50 microns. Metal fibers with
diameters as low as about 0.5 microns and with diameters up to at
least 25 microns have been used quite successfully in the practice
of our invention. It needs to be emphasized that the
aforementioned range is merely illustrative of the success which
is to be contemplated and is more representative of metal fiber

-37-

availability rather than being a limitation on the diameter of metal fibers.

Where the first fiber is a metal, the second fiber may be a metal, a ceramic, carbon, a high surface area material, or any combination of the above. One important subclass of composites results from the second fiber being a metal. The metals which may be employed for the second fiber constitute the same group of metals as may be used for the first fiber as given above and need not be repeated here. The second fiber may be a metal which is the same as or different from that of the first fiber; that is, where the second fiber is a metal it is independently selected from the same group of metals from which the first fiber is chosen. Often the second fiber as a metal will be distinguished by having a diameter different from that of the first fiber. More particularly, relatively large diameter fibers in a network impart strength and structural integrity to the composites. On the other hand, a small diameter second fiber may be chosen to adjust the void volume and porosity of the resulting composite. Where the two metals used are of quite different diameter, it has the effect of constructing a small mesh network on a large mesh framework, which has been found to be a very useful structure. The second fiber may have a diameter ranging anywhere from about 0.001 that of the first fiber to 1000 times that of the first fiber. The second fiber may be present at a weight ratio of from about .001 to about 100 that of the first fiber. It should be clear that adjustment of both the weight ratio as well as the diameter of the second fiber enables one to control the porosity and void volume of the resulting composite almost without limitation and

-38-

essentially continuously and enables one to fabricate articles customized for their intended use. The ratio of fiber length to fiber diameter, or aspect ratio, is yet another independent variable, and in the variant where both the first and second fibers are metals the aspect ratio of the second fiber can range between about 10 and about 10,000.

As shown in the electron micrographs of Figures 9 and 10, application of our invention has allowed us to create a composite, which in this case is an electrode structure, combining both a high void volume and a fine pore size distribution, normally considered to be mutually exclusive electrode properties. The composite of the figures in question is one of staom;ess stee; fibers of two different diameters and lengths. If this composite were electroplated with nickel, or if an analogous composite were prepared from nickel fibers, and thereafter packed with $Ni(OH)_2$ via an electrochemical precipitation technique it would provide an ideal anode structure for the $Ni-H_2$ battery system. In this particular instance, the normally high internal resistance through the less conductive $Ni(OH)_2$ within the voids of a traditional nickel plaque anode is greatly decreased by the attachment of small electrical feed wires which penetrate within the voids formed by the larger nickel (or nickel-coated) fibers. The larger nickel (or nickel-coated) fibers are used for structural support of the smaller fibers and the full embodiment of this application of our invention entails that the complete electrode utilize fibers of at least two different diameters and aspect ratios. The finished electrode has lower mass, higher attainment of its theoretical capacity, greater cycle life, suffers less internal

resistance and allows higher specific energy and power densities. The attributes of this electrode design are directly applicable to other battery systems such as Ni-Cd, Li-SOCl$_2$, Zn-air, etc. Cf. D. L. Britton, "Lightweight Fibrous Nickel Electrodes for Nickel-Hydrogen Batteries," NASA-TM-100958, 1988.

Composites where the framework is of a large diameter metal fiber upon which is constructed a mesh of smaller diameter metal fibers have a multiplicity of uses. For example, the void volume and pore size can be adjusted so as to provide an adjustable pressure drop. In the case of typical chemical upgrading and catalytic applications it may be desired to provide a maximum internal fiber surface area while minimizing pressure drop. In the case of controlled expansion systems needed, e.g., for automotive air bags, a material is desired which can provide Joule-Thompson cooling and controlled expansion of an explosive gas source at the time of an automotive collision. The composites of our invention may provide such a filter of reduced mass and cost and with the flexibility afforded by this invention.

In the case of superconducting magnetic separation materials or screens required for the beneficiation of coal, clay based pigments, etc., high void volumes or capacities, structural integrity (provided by larger fiber diameters) and high magnetic field gradients (provided by smaller fibers) are simultaneously required. In this instance the void volume and structural integrity required of the separator is provided by larger metallic fibers (e.g., 400 grade magnetic stainless steels may be used) while the interstitial regions of the voids formed by these larger fibers are filled with smaller fibers. The smaller radius of

-40-

curvature of these interstitial fibers provides a greater magnetic field gradient so as to attract and retain magnetic impurities with greater force to the separator. In this instance the high void volume provides greater capacity of the separator prior to demagnetization and cleaning.

As another example, structures having metal fibers of differing diameter can be made with particles of a third material entrapped within its voids. Such composites may contain entrapped or entrained particles of carbon, zeolites, metals, silicas, aluminas, zirconias, magnesias, titanias, other metal oxides and mixed metal oxides of high specific surface area, ceramics, salts and/or other fibers of any of the above-noted materials. Figure 11 shows a metal fiber matrix containing 95% alumina-5% silica fibers possessing a specific surface area of 150 m^2/g. Figure 12 shows a mixed metal fiber matrix containing mica platelets entrapped within the matrix and kaolinites chemically attached to the stainless steel fibers through the surface iron impurities in the kaolinite particles. The size of the particles entrapped within the network is not a critical factor, although usually particle size is between about 0.1 and about 5000 microns.

Figure 14 shows how particles can be encapsulated within the network of the articles of this invention and how two different metallic fiber diameters assist in the entrapment of these particles. The material shown in Figure 14 has entrapped particles of a commercial biosupport, although small particles of virtually any supported catalyst or catalyst support can substitute for the biosupport. In particular, the articles of our invention can entrap particles which are impregnated with a metal

or metal compound having catalytic properties. The resulting
material is flexible, can be layered, can be produced in a variety
of shapes and sizes with graded porosities, is electrically
conductive and has a low pressure drop compared to a packed bed.
It therefore has many of the advantages of a fluidized bed
including enhanced heat and mass transport and improved product
control and selectivity, while being much easier to operate than a
fluidized bed since the individual catalyst grains are firmly
attached and cannot be entrained in the product stream at higher
fluid flow rates through the bed. Since the extremely small
catalyst particles can be entrapped within the structure, high
effectiveness factors via reduced intraparticle mass transport
limitations are obtained and overall loadings and costs of
precious metal catalytic reactors can be greatly reduced.

Figure 15 shows the material of Figure 14 which has been
impregnated with growing cells. The material of this invention
can thus function as a biosupport with many of the above noted
mass transport advantages. Additionally, the electrical
conductivity of the metal matrix allows coreactants such as oxygen
to be generated internally through the electrolysis of aqueous
electrolytes. Such procedures facilitate growth and production
rates, and remove inerts such as nitrogen from the system when air
is no longer pumped through the system, thereby reducing expensive
pumping costs. The overall system shows a lower pressure drop
than a packed bed, the flow direction can be readily reversed and
the system is significantly more clog-resistant than a packed bed.
Furthermore, it is expected that many cellular and enzymatic
processes which are enhanced in an applied electric field can be

greatly facilitated by the embodiment of the invention shown in Figures 13 and 14. If particles of a bioseparator or adsorbent are combined into the matrix, then very high conversions might be achieved in the absence of product and feed-back inhibition when the product is absorbed immediately after production within the matrix. Since many of the bioadsorbents are electrically activated, the unique conductivity aspects of the matrix provide a mechanism for discharging products from the matrix and operating the process in a cyclic fashion.

Since many biological processes are envisioned for space applications, the fixed nature of the biosupport particles and the ease with which a highly dispersed gaseous coreactant can be generated within the electrode appear to make this material unusually promising for applications in zero gravity. The ability to generate a gaseous coreactant within a matrix containing a traditional heterogeneous catalyst or electrocatalyst, as discussed above, is also applicable to the area of electroorganic synthesis and it is anticipated that this invention can provide many advantages to this area as well.

As mentioned previously, where the composite is to be used as, for example, an electrode and good electrical contact among the fibers is paramount, then the fibers may be electroplated to enhance such contact. This may be done both in cases where the first and second fibers are metals, as well as in those cases where the second fiber is not a metal, whether or not the second fiber is a conductor such as carbon.

Another important class of composites is that where the second fiber is not a metal but a high surface area material. It

is desirable that such second fibers have a surface area of at least 50 square meters per gram (m^2/g), although materials with a surface area greater than about 100 m^2/g are preferred, and those with a surface area greater than 250 m^2/g are particularly preferred. The minimum surface area needed is 1.5 m^2g. Among such high surface area materials available as fibers are included carbon, silica, magnesia, alumina, clays, titania, aluminosilicates, silicaaluminophosphates, aluminophosphates, and so forth.

Yet another important group of composites are those where the second fiber is a ceramic material. For the purpose of this application a ceramic material is an oxide, nitride, or carbide of metals such as aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, berrylium, iridium, silicon, magnesium, manganese, gallium, and their mixtures. Specific examples of ceramics which may be used in our invention include silica, alumina, silica-aluminas, boron nitride, boron carbide, silicon nitride, silicon carbide, titanium nitride, titanium carbide, titanium boride, zirconium nitride, zirconium carbide, niobium carbide, niobium nitride, molybdenum nitride, molybdenum carbide, tungsten carbide, tantalum carbide, and so forth.

In a variant of our invention the second fiber is porous, for it then may be impregnated with a metal or a metal compound, especially one with catalytic properties for at least one chemical process. This variant is especially suitable where the second

-44-

fiber has a relatively high surface area, as mentioned above, and normally will be practiced in that mode. As previously stated, any metal which exhibits suitable catalytic properties may be used and are illustrated by metals such as aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, berrylium, iridium, silicon, magnesium, manganese, and gallium, as well as their carbides, oxides, sulfides, nitrides, and combinations thereof. The porous second fiber may be impregnated by the metal or metal compound by any means known in the art. Such methods of impregnation include electrochemical precipitation, infiltration and drying, incipient wetness and drying, ion exchange, gas adsorption, liquid absorption, and vapor deposition. Methods of deposition are well known to those skilled in the catalytic art and need not be further elaborated upon.

The composites of our invention can be made by a relatively straightforward, uncomplicated method generally applicable to many types of materials. The fibers, and other components where present, are dispersed in a fluid medium along with an agent which we will refer to as a structure forming agent . The resulting dispersion is then cast into a predetermined shape and the cast dispersion is treated according to the various bonding methods discussed earlier so as to effect bonding of at least the first fibers at a plurality of their junctions. Much, and often substantially all of the structure forming agent (if one is used) is then removed, often coincident with whatever procedure is used

to effect bonding, but sometimes done sequentially, especially when the bonding procedure is followed by chemical or electrochemical leaching of the structure forming agent or pore former. As examples, residual materials can be removed through the use of an appropriate and selective etching organic acid; cores of electroplated carbon fibers can be removed via thermal oxidation, plasma oxidation, etc.; a ceramic particulate or void former can be preferentially removed by an appropriate caustic. Our method is extraordinarily flexible and broadly applicable as to the kinds of fibers which may be used in its practice. It also exhibits virtual universality as to the resulting shape, and in fact net shaped or near net shaped particles may be readily made. The method also manifests some versatility as to bonding methods, which affords great flexibility in processing procedures.

The fibers which may be used in this invention already have been adequately discussed, obviating the need for describing them at this point. These fibers are dispersed in a fluid medium along with other, optional solid and/or liquid components. These optional components are functionally significant in the final composite, becoming entrapped and enmeshed in the network, and occupying what otherwise would be the voids in the resulting composite. Examples of solid particulate components which may be used in the practice of this invention include zeolites, particulate catalysts generally, adsorbents, ceramics, and combinations thereof.

The fibers and other components, if any, are dispersed in a liquid by any suitable means. It is not essential to have a uniform dispersion, although often such uniformity is desirable.

-46-

Dispersion may be effected by such means as sonication, agitation, ball milling, and so forth. The purpose of the liquid is merely to facilitate effective dispersion of the solids, especially where one wants as uniform a dispersion as is feasible in the final preform. Normally the liquid used will be unreactive with the other components of the dispersion, but one can envisage special cases where a functionally desirable reactive property of the medium may be advantageously combined with its fluidity. Since the liquid is later removed it is clear that it should be readily removable, as by volatilization. Water is normally a quite suitable liquid, although water-alcohol mixtures, and especially water-glycol mixtures, may be used. Illustrative examples of other liquids include methanol, ethanol, propanol, ethylene glycol, propylene glycol, butylene glycol, poly(ethylene glycol)(s), poly(propylene glycol)(s), and so forth. Other organic liquids also may be used, but normally without any advantages. Since water is by far the most economical and most universally available liquid it is the one of choice in the practice of our invention. The liquid medium also may contain salts where these are desirable, and the greater solubility of salts in water relative to organic media also make the use of water highly advantageous. While some mixtures of the above noted liquids are used to adjust the viscosity of the dispersion so that filtering or settling onto a screen or filter provides a certain degree of uniformity within the "wet" preform regardless of the densities and drag forces acting on the various particulates, still other additives including surfactants and dispersing agents can be used to assist in the mixing process and also to

-47-

preferentially associate at least two of the solids with one another.

A preform is the solid containing a non-woven dispersion of the fibers and any other optional components either in the structure forming agent or located upon or within the pore volume of one or more of the fibers. The structure forming agent provides a solid matrix in which the fibers and optional components are dispersed. The purpose of the structure forming agent is to permit the fabrication of a solid preform of an otherwise structurally unstable dispersion of the elements of the final composite which can be shaped, stored, and otherwise handled prior to creation of an interlocked network via bonding of at least the first fibers at their junctions. The structure forming agent merely provides a stable, although relatively weak, physical structure which maintains the spatial relationship of the components of the final composite prior to the latter's formation. Although the preform is only a temporary structure, it is an important one in the fabrication of the final composite. The structure forming agents used in the preparation of the preform also may contain adjuncts such as pore and void formers.

A short comment on terminology may be in order. What we have called "structure forming agent" is usually referred to as a "binder" in other contexts. However more descriptive and more familiar may be "binder" and "binding agent", these terms might be confused with the particular notion of "bonding" essential to the description of this invention. It is solely to avoid such confusion that we adopt the somewhat awkward term "structure forming agent."

-48-

The structure forming agents may be chosen to volatilize at least to the extent of 90 weight percent, and sometimes to at least 99 weight percent, under conditions which are neither chemically nor physically detrimental to the fibers and other components in the final composite (but vide infra). The structure forming agent generally has no function in the composite and its presence can be minimal. Among the structure forming agents which may be used in the practice of this invention are cellulose, organic resins such as polyvinyl alcohol, polyurethanes, and styrene-butadiene latex, and thermosets such as expoxies, urea-formaldehyde resins, melamine-formaldehyde resins, and polyamide-polyamine epichlorohydrin resins. Cellulose appears to be a quite desirable structure forming agent because it volatilizes completely at relatively low temperatures with little ash formation and is unreactive toward other components in the preform.

The structure forming agent is present in the preform at a range from about 2 to about 90 weight percent. The minimum amount of structure forming agent is that which is necessary to give a stable preform, that is, one which can be handled, shaped, and so forth, an amount which depends upon fiber loading, fiber size, and so forth. The amount of structure forming agent present in the preform will influence the void volume of the final composite, with the higher structure forming agent content affording a higher void volume, hence the structure forming agent can be used as one independent variable to control this property. We have previously noted that where two metal fibers are used with different fiber sizes, the amount of the smaller sized fiber also may be used to

-49-

vary void volume and pore size. Using cellulose as a structure forming agent example, a range from about 10 to about 60 weight percent of cellulose is typical.

After the dispersion of fibers, optional components, and structure forming agent in a liquid is attained, the solids are collected, as on a mat. Excess liquid may be removed, such as by pressing, and the resulting solid dispersion often is dried, especially where it is to be stored prior to further treatment. Where a thermosetting structure forming agent is used, the temperature of drying is important. But in the more usual case there is nothing particularly critical in the drying process, and drying may be performed in air, under elevated temperatures, or in a flowing gas. The mass also may be compacted to a greater or lesser extent to effect void volume; the greater the compaction, the lower will be the void volume. This affords a third independent means of controlling void volume in the final composite. Still a fourth independent means of controlling the void volume and pore size can be affected by altering the tensile properties and aspect ratios of the fibers used. For example, Figures 15 and 16 are of composites prepared from identical paper preforms containing stainless steel fibers, carbon fibers and cellulose fibers in the relative weight ratios 0.5 : 1.0 : 0.5, respectively. In the case of Figure 16, 2 micron diameter stainless steel fibers were used with a length of approximately 5 mm, whereas in the case of Figure 17, 0.5 micron fibers were employed with an average length of 0.1 mm. As can be noted, the smaller diameter and shorter stainless steel fibers produce a sintered deposit or electrode with a significantly smaller void

-50-

volume and pore size distribution.

The dispersion is cast into a predetermined shape prior to, coincident with, or after drying, with the last named procedure the one most commonly employed. The preform resulting from drying is generally quite flexible and adaptable to shapes of various sorts. Often it is quite convenient to cast the dispersion into sheets which can then be rolled up and stored prior to being treated to effect bonding. The sheets can be stored for long periods of time, can themselves be cast into near net-shaped bodies, and can be used for onsite bonding procedures for the fabrication of various articles. Various types of preform sheets may be stacked upon one another prior to any treatment to effect bonding in order to create thicker composites containing spatially graded compositions, graded porosities, nonconductive separator functions, etc. Alternatively, different shaped preform sheets may be stacked so as to form both two and three dimensional structures for various applications. Metal containing preforms can be, e.g., sintered onto thin metal foils which serve as liquid barriers in the case of bipolar electrode assemblies, or the metal foil may be omitted in the case of flow-through geometries. More complex flow patterns and geometries are also obtainable as cellulose-containing preform sheets can be shaped and glued into "corrugated cardboard" like structures prior to bonding treatment and have been shown to retain their shapes after such treatment.

The cast dispersion is treated principally to effect bonding of at least the first fiber junctions. The method used to effect bonding often has the important secondary or ancillary effect of removing the structure forming agent and the remainder of the

-51-

liquid medium. The removal of the structure forming agent and the remainder of the liquid medium may be a second and discrete step which either precedes or succeeds bonding. For economy of exposition we will subsequently treat methods of bonding as effecting concurrent removal of structure forming agent and remaining liquid, although it needs to be explicitly recognized that this is not necessarily the case.

Among the methods which may be used to bond at least the first fibers at their junctions may be mentioned heating, electroforming, electroplating, and various chemical reactions; the more complete exposition of bonding methods given earlier should be consulted. At least where bonding of metal junctions is sought to be effected, heating is the most effective bonding method and also has the desirable attribute of simultaneously effecting removal of some types of organic structure forming agents and the remaining liquid. Heating produces sintering of metal-metal junctions and also ceramic-ceramic junctions, but is not necessarily effective with other fibrous material. Another useful bonding method which may be employed is electroplating. Other methods of bonding have been described earlier.

Structure forming agent generally will be removed via methods which will include volatilization (both sublimation and evaporation), carbonization, other chemical reactions affording volatile products (or gasification generally), acid or caustic leaching, and dissolution, whether dissolution of the structure forming agent per se or of secondary products resulting from chemical degradation or transformation of the structure forming agent. Volatilization as by heating in a suitable atmosphere is

-52-

the most general method of structure forming agent removal and is highly favored in the practice of our invention.

The foregoing description was couched in terms of a structure forming agent which was largely subsequently removed. In another large class of composites the structure forming agent need not be largely removed, and sometimes their removal is undesirable. For example, one may employ as a structure forming agent a polymer which subsequently undergoies carbonization but not volatilization. The resulting composite is then a network of bonded fibers in a graphitic matrix. As another example, in appropriate circumstances it is possible to have a solvated metal salt as a structure forming agent, which is later reduced to lock the structure together. What is important to recognize is that however important may be the class of structure forming agents which are largely removed by subsequent treatment it is not the sole class of structure forming agents which may be used in the practice of our invention.

We have previously noted that the composites of our invention have many diverse uses, and in this section we elaborate upon several of such applications. It needs to be borne in mind that the applications described in this section are only illustrative examples of a large universe of uses and are not intended to be exhaustive or complete. Nor is the presence (or absence) in this section of a particular application meant to denote the relative importance of that application.

Liquid Double Layer Capacitors: High surface area conductive electrodes have been made (see Figures 15 and 16) which have the ability to store large amounts of electrical energy in the polarized

-53-

double layer when such electrodes are immersed in a suitable liquid or solid electrolyte. Such energy can be readily retrieved as electrical energy upon demand depending upon the structure of the device and the physical properties of the materials and electrolytes employed.

Fuel Cells: High surface area fibrous structures are employed as fuel cell electrodes using liquid or solid electrolytes. In the case of liquid electrolytes, our invention allows a high porosity-high void volume structure to be created which assists heat and mass transfer at the electrode (i.e. fibers(s)) surface when electrolytes/reactants are transported through rather than over the electrode surface (i.e., flow direction is perpendicular rather than parallel to the sheet surface). Our electrode design, because of its fuzzy nature, also works better even when the flow direction is parallel to the sheet or stagnation flow exists. In general the performance enhancement results because our fibrous structure permits a self-supporting electrode to be created with high void volume so that the irregular channels retained in the structure permit ready electrolyte/reactant transport inside the structure. Traditional electrodes of lower void volume only employ the outermost regions of their structures to facilitate chemical reaction because of mass transport limitations. Figure 18 shows a plot of how our electrode design outperforms a commercial fuel cell electrode even though our material weighs less and does not contain a precious metal catalyst! These data were collected under conditions of stagnation flow and even greater enhancements would be expected should we flow the electrolytes through our design. Incidentally, traditional electrodes cannot be used in a flow

-54-

through design because of the associated pressure drop and low void volume.

In the case of solid polymer electrolytes, power density in hydrogen-oxygen fuel cells is restricted by the interfacial contact between the catalyst phase and the proton conducting membrane. In our invention, the catalyst is of a fuzzy nature which permits it to be hot pressed into the membrane at one end with the free ends of the fibers extending into the gas phase. When small platinum crystallites (ca. 2.0 nm) are affixed onto these fibers, hydrogen gas can be dissociated on the metal and the hydrogen atoms transported down the carbon fibers via surface diffusion/spillover into the membrane and toward the other electrode where they combine with oxygen to form water and electricity. The extension of the fuzzy surface into the gas phase assists transport of hydrogen atoms toward the other electrode just as high surface area grass blades assist the various metabolic processes which occur in the soil.

Batteries: Because   our   process   allows   us   to   create mechanically tough electrode structures, with high/adjustable void volumes utilizing an array of different materials, it is ideally suited for battery applications, particularly those where the power levels (i.e., the rate of discharge) is limited by solid products which can block access to the interior surface area of the electrode. For example, using normal electrodes $Li-SOCl_2$ batteries experience "cathodic clogging" at about 10 mA/cm_2. In test studies shown in Table 1 under Example 8 it is clear that the good mass transport and high void volume of our structures allows them to operate at somewhere between 15- and 27-fold higher current densities prior to clogging and loss in surface area. These

advantages should also be available to many other battery systems where similar problems are encountered.

Figures 9 and 10 show a structure prepared of high void volume so that it can accommodate precipitates. Also, the use of a second smaller metal fiber allows us to electrically contact the precipitate within these voids when it is desired to discharge or recharge this electrode. Enhanced electrical contact means greater efficiency, reduced internal resistance, greater capacity, higher discharge rates, improved cycle life, etc. This improvement is required in Ni-Cd and in Ni-H_2 batteries, among others.

Hybrid Devices: These combine the attributes of fuel cells or batteries with the double layer capacitor. In other words, pulsed discharge of one of the former devices can give rise to big power surges when power is released from both the Faraday process as well as the energy stored in the double layer.

Filters and Separators: Our process provides a unique and inexpensive means for producing nonwoven articles of various materials and of high uniformity. The resulting composites are particularly well-suited as filter materials of various pore size. Also our composite can be made electrically conductive to assist separations of charged or polarizable species.

Bioseparations are typically performed by 5-20 nm pore size silica-alumina materials which selectively absorb proteins and other biological materials into their pore structures. Electric fields are known to greatly assist this separation on the basis of the charges and polarizabilities of these materials. One problem with silica-alumina materials is pressure drop in packed beds and the insulating nature of these separation materials. Since our process

-56-

can combine metal fibers and particles of bioseparation materials, it has the ability to readily apply electric fields as well as separate particles for lower pressure drop and clog resistance. Flow fields can be easily reversed to unclog filters without washing away the separator, flow rates can be increased to reduced boundary layer diffusion resistance and electric fields can be turned on and off to release or entrain proteins as required.

There are numerous other types of electrosorption separation processes which can be accomplished with our material. Consider for example that carbon based materials among others can be used to selectively adsorb alcohols from complex mixtures. When these processes are performed in a packed bed the rate of separation and removal is limited by diffusion within the bed and boundary layer diffusion above the surface of the bed. In the case of our material a flow through approach is possible so that materials can be quickly absorbed or quickly released once the electric potential is removed. This advantage could be used to reduce the time and costs of separations. Alternatively, consider the merits of a process such as alcohol fermentation using a composite of our invention containing both immobilized yeast cells and an alcohol adsorbent. Not only can the electrolysis of water be used to provide oxygen to the yeast, but the products of reaction can be simultaneously absorbed so as to push the process toward much higher conversions than the living cells would normally tolerate. This is just one example of how a biological system could be pushed past its feedback inhibition point in terms of reaction selectivity. Other examples could also involve pushing reaction equilibria past equilibrium yields by selective electroabsorption of the product. There are a

great many reaction systems where this approach would be applicable including many of those currently under development as part of membrane reaction systems.

The case of magnetic separation systems has already been described. Small fibers mean high magnetic gradients and strong attraction forces; large fibers mean higher void volumes, mechanical integrity and larger capacities prior to demagnetization and shaking. Therefore, our combination of small and large metallic fibers are meritorious for magnetic separations.

Heterogeneous Catalysts Supports: Our materials will provide low pressure drop, the attributes of a fluidized bed while the bed remains stationary regardless of fluid velocity, the ability to change fluid flow directions, high mass and heat transport rates, the ability to encapsulate particles of almost any supported or unsupported heterogeneous catalyst, the ability to use encapsulated materials as electrocatalysts because of the connecting wires, increases in the electrical conductivity of poorly conductive materials by virtue of the metallic fibers (i.e., new types of electrocatalyst support materials), high thermal stability depending on the constituent materials, the ability to provide the internal generation of some reactants via the electrolysis of an appropriate solvent, the ability to be cast in various shapes and sizes! The foregoing features, alone or in combination, are very attractive attributes for catalyst supports.

Bioelectrocatalysts: Figures 13 and 14 depict the situation as earlier described. In summary, the composites of this invention may be used to: (i) provide low pressure drops, (ii) immobilize cells in the absence of abrasion or wash-out from the reactor, (iii) provide

-58-

higher local cell concentrations than available in a pure liquid system, (iv) entrap almost any biosupport, (v) provide internal generation of oxygen or other reactants via electrolysis of a solvent or electrolyte, (vi) provide high growth rates, production rates, reaction rates and enzymatic activities through electric field enhancements, (vii) provide clog resistance, (viii) provide simultaneous incorporation of a selective absorbent of a size exclusive or electrical nature, (ix) provide easy fabrication in various sizes, (x) provide the ability to change flow direction or increase flow velocity, (xi) carry out reactions in zero gravity environments where two phase flows, gas-liquid mixing and immobilization are all required and often prove difficult.

Sensors/Adsorbents: Carbon blacks are one of the most common types of adsorbent/absorbent/filter material employed. The high surface area carbon fibers when utilized in our process may be considered to be carbon black. Our process provides a composite ideally suited for absorbent applications which is well-packaged, has low pressure drop, etc., and which can be electrically characterized as a function of time. Since the electrical properties change with absorption, we can use the electrical characteristics to continually assess the state-of-health of the absorption material and determine its remaining capacity. This attribute makes our material well-suited to reducing costs and enhancing the logistics of systems which require filtration. For example, the military maintains a large supply of carbon black filter cartridges for chemical warfare applications which it periodically throws away or regenerates for logistical purposes. Obviously, a state-of-health indicator for the bed would be greatly

appreciated.

Preforms for Advanced Composites: Since our material can be readily shaped prior to or during processing to effect bonding, it has the ability to provide near-net-shape to fiber-reinforced composite preforms. Furthermore, our large choice of fibers adds a great deal of flexibility, while the nonwoven, 3-dimensional nature of our composite provides toughness in all three directions. In other words, delamination problems normally encountered with traditional carbon-carbon composites employing sheets of graphite fabric reinforcement can be reduced when our material is employed.

For applications requiring controlled interactions with microwaves, cloaking, EMP, RFI, EMI, etc., the conductivity and performance of resultant materials can be controlled by the composition of the fibers, their relative loadings, their aspect ratios, the conductivity and inter-connected nature of the preform, and so forth. The degree of flexibility offered by our process toward the above-noted material design goals is significant and not obtainable by other means.

Waste Water/Effluent Treatment: Many of the above-noted properties are directly applicable here including tailored pore size, secondary materials inclusion for various applications/benefits, low pressure drop/high throughputs, flow reversal, clog resistant, easy regeneration, generation of internal reactants via electrolysis (Cl_2, O_2, H_2O_2, etc.) creation of internal electric fields providing enhancements in growth, decomposition, filtration, separation, coalescence, etc., ability to fabricate in large scale quantities which are mechanically tough and flexible, and so on.

-60-

EXPERIMENTAL

The following description is representative of the preparation of the composites prepared within. Differences in materials, conditions, etc., will be indicated for the individual composites where appropriate.

Materials--The constituent materials employed during composite preparation included carbon fibers from Charcoal Cloth, Ltd., 316L stainless steel fibers from Bekaert Steel Wire Corp. and/or National Standard, cellulose fibers as a mixture of soft and hard woods, and 316L stainless steel foils from Arnold Engineering. Individual carbon fibers were 2-3 microns in diameter but were used in the form of 20 micron diameter bundles up to 5 mm in length containing ca. 30 individual fibers. Cellulose fibers were 20-30 microns in diameter and varied in length from 100 to 1000 microns. The stainless steel foils were 5 microns in thickness.

Fiber preparation--Before the various fiber materials could be combined into a paper preform, the carbon and stainless steel fibers required separation and dispersion into a slurry for easy mixing with other materials. In raw form, the carbon fibers were bundled and twisted into strands and woven into charcoal cloth. The "cloth" was dismantled into strands, then cut into 0.5 cm sections to allow for dispersion of individual fiber bundles in water. "As received" stainless steel fibers were coated with polyvinyl alcohol (PVA) type Mowiol 4-88, which was utilized during sizing and cutting prior to shipment. PVA was removed by repeated rinsing of these fibers in distilled water.

Formation of paper preform--Since physical mixtures of the

fibers are not mechanically stable, cellulose fibers were employed as a binder to form paper preforms. The paper preforms used in composite preparation were processed according to TAPPI Standard 205 using Noran equipment. The pretreated fibers along with cellulose fibers were agitated at 50 Hz in 1 liter of water for five to twenty minutes. The dispersed fiber mixture was then collected on a sheet mold (200 cm^2) to form the wet paper composite preform. The preform was pressed at ca. 400 kN/m^2 and allowed to dry in air at room temperature.

Assembly of electrode preforms--The first fiber-second fiber-cellulose composite papers (i.e., paper preforms) and stainless steel foils were cut into circular disks with diameters of 13 and 19 mm respectively, and assembled by layers. In most cases, an optional 19 mm diameter sheet of stainless steel-cellulose paper preform was placed on top of each side of the composite structure to serve as a protective layer.

Sintering of electrode preforms--The layered electrode preform was placed between two quartz plates (20 x 30 mm), which were held in place by a quartz clip. The sample was placed in a controlled atmosphere quartz U-tube reactor (25 mm diameter) for heat treatment. The sintering reactor was equipped with flexible gas lines to facilitate movement of the reactor into and out of the vertical sintering furnace (Heviduty, 10 A, 1150 W). Sintering was performed in a reducing atmosphere of H_2 with a flow rate of 10-100 cc/min (STP) and total pressure of 101 kPa. Gases were supplied by Liquid Air with purities of 99.995% for H_2. Gas flow was monitored using a Linde Model FM-4550 flow controller.

The feed gas mixture was passed over Cu turnings at ca. 500 K

-62-

to remove background CO, CO_2, O_2 and H_2O and then passed through a molecular sieve trap immersed in a liquid N_2 trap to further remove background condensibles. The sintering reactor was passivated with feed gas for a minimum of three hours prior to reaction. The sintering furnace was preheated to 1423 K prior to beginning each experiment. The reactor was then introduced into the furnace causing a rapid cooling of the furnace to ca. 1400 K. The experimental temperature was typically reached in 5-7 min followed by sintering at the desired temperature. The sintering reactor was quenched by rapidly removing it from the furnace.

Example I. A mixed-fiber composite was made from 2 μm diameter and 0.5 m diameter 316 stainless steel (ss) fibers combined in equal weight fractions. The length of the 2 m fibers added to the preform were 5 mm, the length of 0.5 μm fibers were ca. 100 μm. The electrodes of Figures 9 and 10 were prepared by casting a 16 cm diameter, circular preform sheet, using 0.5 g of 2 μm diameter 316 stainless steel fibers, 0.5 g of 0.5 μm diameter 316 stainless steel fibers, and 0.5 g of cellulose fibers. The fibers were mixed at 50 Hz agitation in 1 liter of water prior to settling onto a filtration screen. The preform sheet was pressed at 400 kN/m^2, dried in air for >24 hours and sinter bonded at 1323K for 20 minutes in 101 kPa of H_2.

Example 2. The electrode of Figure 11 was prepared by casting a 16 cm diameter circular preform sheet, 0.5 g of 2 μm diameter 316 stainless steel fibers, 0.5 g of 0.5 μm diameter 316 stainless steel fibers, 0.5 g of cellulose fibers and 0.5 g of a commercially available alumina-silica fiber, Saffil, obtained from ICI Chemicals. Saffil is 95% alumina and 5% silica, Saffil fibers are 3 ± 1 μm in

diameter and have a surface area of 150 m^2/g. The length of the 2 μm steel fibers was 5 mm, the length of the 0.5 μm ss fibers was 100 μm. The fibers were mixed at 50 Hz agitation in 1 liter of water prior to settling onto a filtration screen. The preform sheet was pressed at 400 kN/m^2, dried in air for >24 hours and sinter bonded at 1323K for 20 minutes in 101 kPa of pure H_2.

Example 3. The composite of Figure 12 was prepared by casting a 16 cm diameter circular preform sheet using 0.5 g of 2 μm diameter 316 stainless steel fibers, 0.5 g of 0.5 μm diameter 316 stainless steel fibers, 0.5 g of cellulose fibers, and 0.5 g of a filler clay (Hi White, available from Huber Clays Inc.) The length of the 2 μm ss fibers was 5 mm, the length of the 0.5 μm ss fibers was 100 μm. The preform sheet, prepared as described in the earlier examples, was pressed at 400 kN/m^2, dried in air for >24 hours and sinter bonded at 1323K for 20 minutes in 101 kPa of pure H_2.

Example 4. The composite of Figures 13 and 14 were prepared by casting an 16 cm diameter, circular preform sheet, using 0.5 g of 2μm diameter 316 stainless steel fibers, 1.0 g of 0.5 μm diameter 316 stainless steel fibers, 2.0 g of cellulose fibers and 2.5 g of a commercially available biosupport known as Biofix available from English China Clays. The length of the 2 μm ss fibers was 5 mm, the length of the 0.5 μm ss fibers was 100 μm. The liquid used was water combined with a cationic retention aid was obtained from Betz Paper Chemicals which assisted the biosupport in associating with the cellulose fibers while in an aqueous solution. The preform sheet was prepared, pressed, dried, and sintered as described in the prior example. Figure 15 is a photomicrograph of material prepared by circulating a solution containing yeast cells through the

-64-

composite described above. The cells shown in the Figure have become entrapped within the matrix and the resulting composite can now be used, for example, as an enzyme reactor, or for fermentation employing a steady-state cell population.

Example 5. The composite of Figure 16 was prepared by casting a 16 cm diameter circular preform sheet, using 0.5 g of 2 μm diameter 316 stainless steel fibers, 1.0 g of 2 μm diameter carbon fibers and 0.5 g of cellulose fibers. The length of the 2 μm ss fibers was 5 mm. The carbon fibers were cut to a length of 5 mm and had a surface area of ca. 800 m^2g. These fibers were left in the form of ca. 10 μm bundles containing ca. 30 fibers per bundle. The preform sheet was prepared, pressed, dried, and sintered as described in the prior example.

Example 6. The composite of Figure 17 was prepared by casting a 16 cm diameter circular preform sheet, using 0.5 g of 0.5 μm diameter 316 stainless steel fibers, 1.0 g of 2 μm diameter carbon fibers described in the prior example, and 0.5 g of cellulose fibers. The length of the 0.5 μm ss fibers was 1000 μm. The preform sheet was prepared, pressed, dried, and sintered as described in the prior example.

Example 7. A commercially available electrode material, Prototech, available from Electrosynthesis Inc. of East Amherst, New York, was purchased as a 24 mg/cm^2 sheet containing 10 weight percent supported Pt crystallites and a porous Teflon separator material as a backing and used as the commercial reference.

Our material labeled as "Composite" was prepared by casting a 16 cm diameter, circular preform sheet, using 1.0 g of 2 μm diameter 316 stainless steel fibers, 1.0 g of 2 μm diameter carbon fibers and

-65-

0.5 g of cellulose fibers. The length of the 2 μm ss fibers was 5 mm. The preform sheet was prepared, pressed, dried, and sintered as described in the prior example.

To produce the electrode shown in Figure 18, one piece of the preform sheet prepared above was cut into a 1.3 cm diameter circular piece and sandwiched between two 1.9 cm diameter pieces of a masking and protective preform which contained only stainless steel and cellulose fibers. The preform sheet for the latter pieces was prepared identically to the preform sheet for the active layer except that the carbon fiber bundles were omitted and the mass of stainless steel fibers and cellulose fibers per sheet were both 0.5 g. The resulting stack of three sandwiched preform pieces was sinter bonded at 1323K for 30 minutes in 101 kPa of pure H_2 to afford an article of density 16 mg/cm^2 which contained no Pt. The stainless steel layers on each side of the electrode served as a protective layer to protect the carbon-containing layer from any type of mechanical abrasion.

The data in Figure 18 is a comparison of polarization data between our electrode and the commercial product. At low current densities the commercial product is superior. However, at higher current densities our electrode shows less polarization losses, even though our material does not contain Pt. The open structure of our material permits greater mass transport than the commercial material. The low void volume and porosity of the commercial product does not allow its active Pt materials to participate in the reaction at high reaction rates, whereas the inherent activity of the carbon, when accessible, is more than enough to overcome the presence of Pt at high reaction rates, as demonstrated by our

-66-

electrode material.

Example 8. The material described in Example 5 was subsequently electroplated with Ni from a $NiSO_4-6H_2O$ solution at the indicated current densities and times. The 21 weight percent carbon in the sintered electrode, rather than the expected 67% from the preform composition, reflects the fact that the preform was sintered onto a 316 ss foil and that some of the carbon was gasifed during sintering. Performance data are summarized in Table 1.

Table 1.   Nickel Electrodeposition into Composite Electrode

Amount of Carbon in Composite electrode: 0.00582 gm (20% carbon by weight)

Geometric Electrode area : 1.27 cm^2

Plating Solution : 0.2 M $NiSO_4.6H_2O$

Counter Electrode : Platinum mesh

Reference electrode : SCE

Applied Current Density (mA/cm^2)	Time Held (mins)	Total Voltammetric Charge (cc⁓./gm)
--	--	1.79
27.6	10	2.61
55.1	5	2.80
78.7	5	2.90
157.5	6.7	2.85
236.0	6.7	0.395
275.0	6.7	0.347

The column marked "Total Voltammetric Charge" (coul/gm) is based on the weight of carbon only and does not include contributions from the ss foil or ss fibers. The increasing values in this column indicate how electrodeposition initially causes greater contact between carbon and ss, while at higher current densities and longer times the decrease is due to a blockage of the active material by a nickel overlayer (i.e., look at the micrograph). Overall, our material functions at between 15 to 27 times higher current densities than current commercial cathodes.

-68-

WHAT IS CLAIMED IS:

1. An article comprising a network of a first fiber and at least one second fiber, where at least said first fiber has a plurality of bonded junctions at the first fiber crossing points.

2. The article of Claim 1 where the first fiber is a metal and the second fiber is selected from the group consisting of the first metal, a second metal, a ceramic, a high surface area material, carbon, or any combination thereof.

3. The article of Claim 1 where at least the second fiber has a surface area from 1.5 to about 1500 square meters per gram.

4. The article of Claim 3 where the fiber is selected from the group consisting of silica, carbon, magnesia, alumina, titania, aluminosilicates, aluminophosphates, silicaaluminophosphates, and clays.

5. The article of claim 3 where the second fiber has a surface area of at least 50 square meters per gram.

6. The article of Claim 1 where the first fiber is a metal,or any combination of metals, selected from the group consisting of aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, berrylium, iridium, silicon, magnesium, manganese, gallium and their alloys.

7. The article of Claim 2 where the second fiber is a metal.

8. The article of Claim 7 where the metal of the first fiber and the metal of each of the second fibers is independently selected from the group consisting of aluminum, titanium, vanadium, chromium,

-69-

iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, berrylium, iridium, silicon, magnesium, manganese, gallium and their alloys.

9. The article of Claim 7 where the second fiber has a diameter from about 0.001 to about 1000 times that of the first fiber.

10. The article of Claim 9 where the second fiber has an aspect ratio between about 10 and about 10,000.

11. The article of Claim 7 where the second fiber is present at a weight ratio of from about 0.001 to about 100 that of the first fiber.

12. The article of Claim 1 where at least the first fiber is electroplated.

13. The article of Claim 1 where at least the first fiber has a conductive coating.

14. The article of Claim 1 where the first fiber is a metal and the second fiber has a surface area of from 1.5 to about 1500 square meters per gram.

15. The article of Claim 14 where the second fiber is selected from the group consisting of silica, carbon, magnesia, alumina, titania, aluminosilicates, aluminophosphates, silicaaluminophosphates, and clays.

16. The article of Claim 2 where the second fiber is a ceramic selected from the group consisting of the oxides, carbides, and nitrides of aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum,

tungsten, rhenium, osmium, platinum, gold, antimony, berrylium, iridium, silicon, magnesium, manganese, and gallium and mixtures thereof.

17. The article of Claim 3 or Claim 14 where at least the second fiber is impregnated with a third metal or a compound thereof, said third metal selected from the group consisting of aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, berrylium, iridium, silicon, magnesium, manganese, and gallium.

18. The article of Claim 1 further characterized in having entrapped within the network particles whose size is between about 0.1 to about 5000 microns.

19. The article of Claim 18 where said particles are impregnated with a metal or metal compound having catalytic properties.

20. A composite comprising a matrix of carbon fibers interwoven in a network of fused metal fibers.

21. The composite of Claim 20 where the composite contains from about 1% to about 98% by weight of carbon fibers.

22. The composite of Claim 20 where the carbon fibers have a diameter from about 20 nm to about 1 mm.

23. The composite of Claim 20 where the carbon fibers have a surface area between 1 and about 1500 square meters per gram.

24. The composite of Claim 23 where the carbon fibers have a surface area between about 50 and 1350 square meters per gram.

25. The composite of Claim 24 where the carbon fibers have a surface area between about 250 and about 1000 square meters per

gram.

26. The composite of Claim 20 further characterized in having a surface area from about 0.001 to about 1350 square meters per gram.

27. The composite of Claim 20 where the metal fibers have a diameter from about 1 to about 10 microns.

28. The composite of Claim 20 containing from about 20 to about 98% carbon fibers.

29. The composite of Claim 20 where the metal is selected from the group consisting of aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, beryllium, iridium, silicon, and combinations thereof.

30. The composite of Claim 20 where the metal is a conducting alloy.

31. The composite of Claim 30 where the conducting alloy is selected from the group consisting of constantan, hastelloy, nichrome, inconel, monel, carpenter's metal, stainless steels, other steels, and other iron alloys.

32. The composite of Claim 31 where the conducting alloy is a stainless steel.

33. An article comprising a plurality of layers where each layer is a network of Claim 1.

34. An article of manufacture comprising a dispersion of a first fiber, at least one second fiber, and an organic structure forming agent.

35. An electrode comprising a composite bonded to an

electrically conducting material, where the composite comprises a
matrix of carbon fibers interwoven in a network of fused metal
fibers.

36.   The electrode of Claim 35 where the composite contains
from about 1 to about 98% by weight of carbon fibers.

37.   The electrode of Claim 35 where the carbon fibers have a
diameter from about 20 nm to about 1 mm.

38.   The electrode of Claim 35 further characterized in having
a surface area from about 0.001 to about 1350 square meters per
gram.

39.   The electrode of Claim 35 where the carbon fibers have a
surface area between 1 and about 1500 square meters per gram.

40.   The electrode of Claim 39 where the carbon fibers have a
surface area between about 50 and 1350 square meters per gram.

41.   The electrode of Claim 40 where the carbon fibers have a
surface area between about 250 and about 1000 square meters per
gram.

42.   The electrode of Claim 35 where the metal fibers have a
diameter from about 1 to about 14 microns.

43.   The electrode of Claim 35 containing from about 20 to
about 98% carbon.

44.   The electrode of Claim 35 where the metal is selected from
the group consisting of aluminum, titanium, vanadium, chromium,
iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum,
ruthenium, rhodium, palladium, silver, cadmium, indium, tin,
hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold,
antimony, beryllium, iridium, silicon, and combinations thereof.

45.   The electrode of Claim 35 where the metal is a conducting

alloy.

46. The electrode of Claim 35 where the conducting alloy is selected from the group consisting of constantan, hastelloy, nichrome, inconel, monel, carpenter's metal, stainless steels, other steels, and other iron alloys.

47. The electrode of Claim 46 where the conducting alloy is a stainless steel.

48. The electrode of Claim 29 where the electrically conducting material is a second metal and the composite is bonded to said second metal by sintering.

49. A preform for a composite comprising a dispersion of carbon fibers, metal fibers, and an organic binder, where said organic binder is at least 90% volatilized at temperatures sufficient to fuse the metal fibers with a loss of less than about 25 weight percent carbon.

50. The preform of Claim 49 where the binder is cellulose.

51. The preform of Claim 49 where the binder is an organic resin.

52. The preform of Claim 51 where the resin is selected from the group consisting of polyurethanes, polyvinyl alcohols, epoxy resins, styrene-butadiene latex, urea-formaldehde resins, melamine-formaldehyde resins, and polyamide-polyamine epichlorohydrin resins.

53. The preform of Claim 49 where the binder is present in an amount from about 2 to about 80 weight percent of the total preform.

54. The preform of Claim 53 where the binder is cellulose present in an amount between about 10 and about 60 weight percent.

55. The preform of Claim 54 where the binder is at least 99 weight percent volatilized at temperatures sufficient to fuse the

metal fibers with a loss of less than about 25 weight percent carbon.

56. The preform of Claim 42 where the binder is at least 99 weight percent volatilized at temperatures sufficient to fuse the metal fibers with a loss of less than about 5 weight percent carbon.

57. A method of making a shaped article having a network of a first fiber and at least one second fiber, where at least said first fiber has a plurality of bonded junctions at the first fiber crossing points, said method comprising forming a dispersion of the fibers, optional components, and at least one structure forming agent in a liquid, casting the dispersion into a predetermined shaped preform, treating the cast dispersion to effect bonding of at least the first fibers at a plurality of the first fiber junctions, and recovering the shaped article.

58. The method of Claim 57 where the first fiber is a metal and the second fiber is selected from the group consisting of the first metal, a second metal, a ceramic, a high surface area material, carbon, or any combination thereof.

59. The method of Claim 57 where at least the second fiber has a surface area from 1.5 to about 1500 square meters per gram.

60. The method of Claim 59 where the fiber is selected from the group consisting of silica, carbon, magnesia, alumina, titania, aluminosilicates, aluminophosphates, silicaaluminophosphates, and clays.

61. The method of claim 59 where the second fiber has a surface area of at least 50 square meters per gram.

62. The method of Claim 57 where the first fiber is a metal, or any combination of metals, selected from the group consisting of

aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, berrylium, iridium, silicon, magnesium, manganese, gallium and their alloys.

63. The method of Claim 58 where the second fiber is a metal.

64. The method of Claim 63 where the metal of the first fiber and the metal of each of the second fibers is independently selected from the group consisting of aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, berrylium, iridium, silicon, magnesium, manganese, gallium and their alloys.

65. The method of Claim 63 where the second fiber has a diameter from about 0.001 to about 1000 times that of the first fiber.

66. The method of Claim 65 where the second fiber has an aspect ratio between about 10 and about 10,000.

67. The method of Claim 63 where the second fiber is present at a weight ratio of from about 0.001 to about 100 that of the first fiber.

68. The method of Claim 57 where at least the first fiber is electroplated.

69. The method of Claim 57 where at least the first fiber has a conductive coating.

70. The method of Claim 57 where the first fiber is a metal and the second fiber has a surface area of from 1.5 to about 1500 square

-76-

meters per gram.

71. The method of Claim 70 where the second fiber is selected from the group consisting of silica, carbon, magnesia, alumina, titania, aluminosilicates, aluminophosphates, silicaaluminophosphates, and clays.

72. The method of Claim 58 where the second fiber is a ceramic selected from the group consisting of the oxides, carbides, and nitrides of aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, berrylium, iridium, silicon, magnesium, manganese, and gallium and mixtures thereof.

73. The method of Claim 59 where at least the second fiber is impregnated with a third metal or a compound thereof, said third metal selected from the group consisting of aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, berrylium, iridium, silicon, magnesium, manganese, and gallium.

74. The method of Claim 57 where the cast dispersion is treated so as to remove at least 90 percent of the structure forming agent.

75. The method of Claim 57 where the structure forming agent is selected from the group consisting of cellulose, polyvinyl alcohol, polyurethanes, styrene-butadiene latex, epoxy resins, urea-formaldehyde resins, melamine-formaldehyde resins, and polyamide-

polyamine epichlorohydrin resins.

76. The method of Claim 74 where the structure forming agent is cellulose.

77. The method of Claim 57 where the method of treating the cast dispersion to effect bonding is selected from the group consisting of heating, electroforming, electroplating, chemical vapor deposition, reactive plasma spraying.

78. The method of Claim 57 further characterized in that said preform is compacted under pressure prior to being treated to effect bonding.

79. A method of making a composite comprising preparing a uniform dispersion of carbon fibers, metal fibers, and a solid binder in a liquid medium, collecting the wetted uniform solid dispersion, removing the liquid medium from the solid dispersion to afford a dried preform, heating the dried preform in an atmosphere containing hydrogen at conditions sufficient to volatilize at least 99% of the binder and fuse the metal fibers, with a weight loss of under about 15 weight percent of carbon fibers, and recovering the resultant composite.

80. The method of Claim 79 where the metal is selected from the group consisting of aluminum, titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, hafnium, tantalum, tungsten, rhenium, osmium, platinum, gold, antimony, beryllium, iridium, silicon, and combinations thereof.

81. The method of Claim 79 where the metal is a conducting alloy.

82. The method of Claim 81 where the conducting alloy is

selected from the group consisting of constantan, hastelloy, nichrome, inconel, monel, carpenter's metal, stainless steels, other steels, and other iron alloys.

83.   The method of Claim 82 where the conducting alloy is a stainless steel.

84.   The method of Claim 79 where the binder is cellulose.

85.   The method of Claim 79 where the binder is an organic resin.

86.   The method of Claim 79 where the resin is selected from the group consisting of polyurethanes, polyvinyl alcohols, epoxy resins, styrene-butadiene latex, urea-formaldehde resins, melamine-formaldehyde resins, and polyamide-polyamine epichlorohydrin resins.

87.   The method of Claim 79 where the binder is at least 99 weight percent volatilized at temperatures sufficient to fuse the metal fibers with a loss of less than about 25 weight percent carbon.

88. The preform of Claim 79 where the binder is at least 99 weight percent volatilized at temperatures sufficient to fuse the metal fibers with a loss of less than about 5 weight percent carbon.
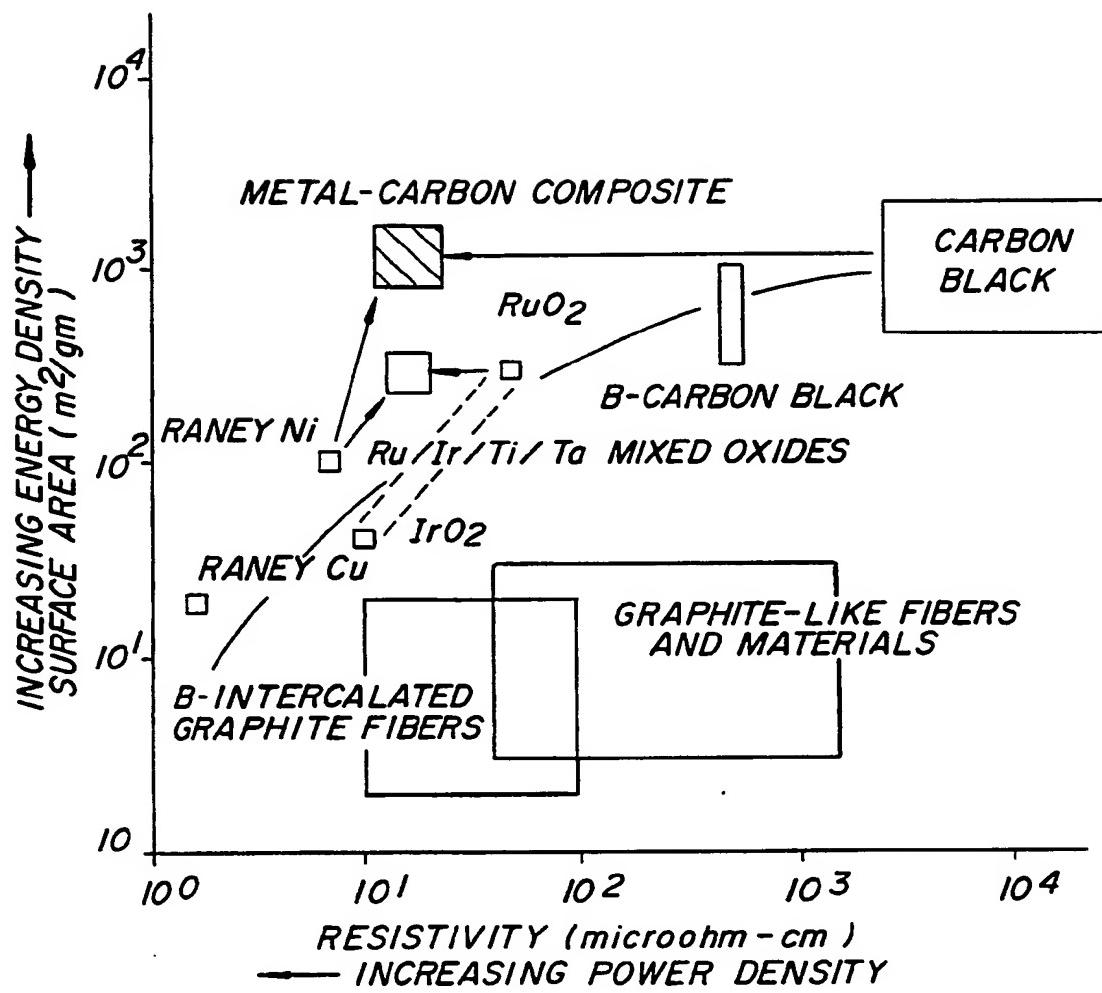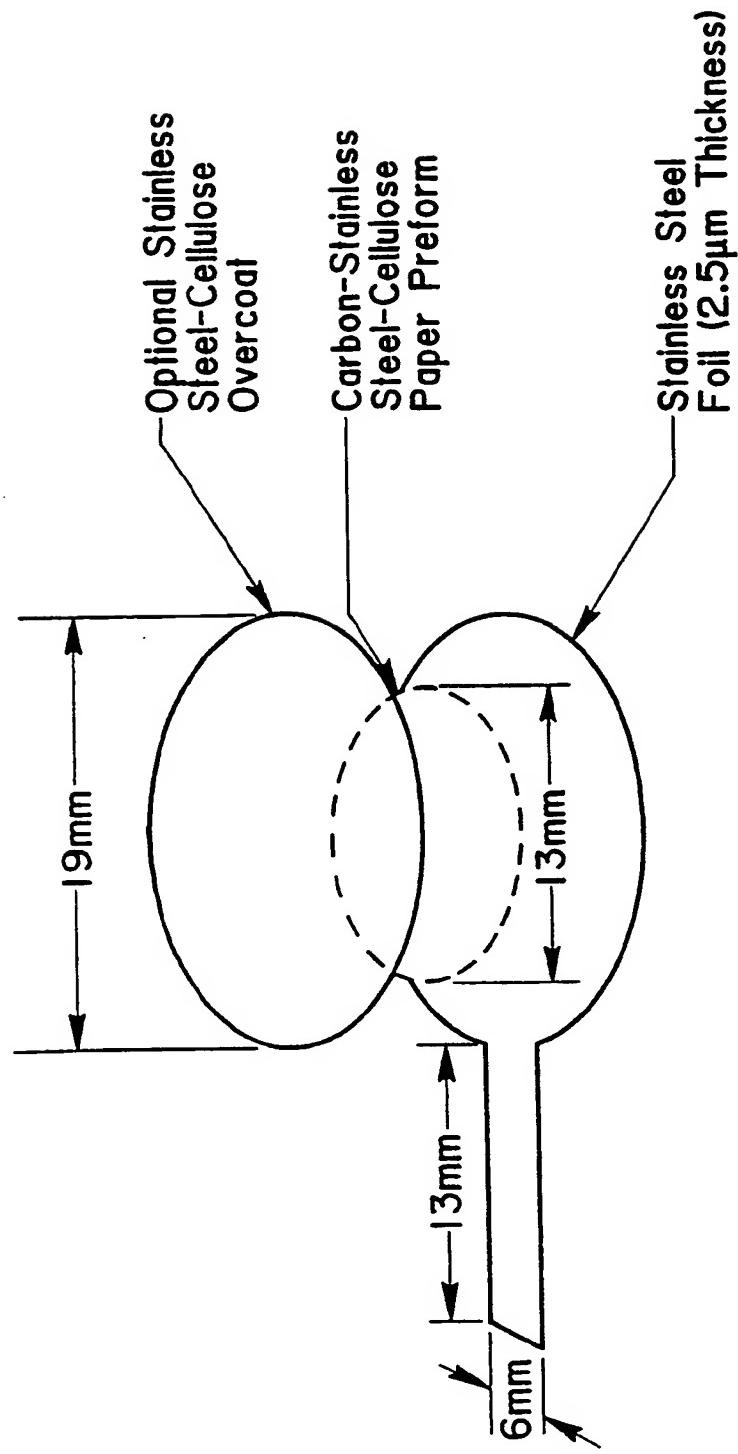
FIG. I

FIG. 2

FIG.3

FIG.4
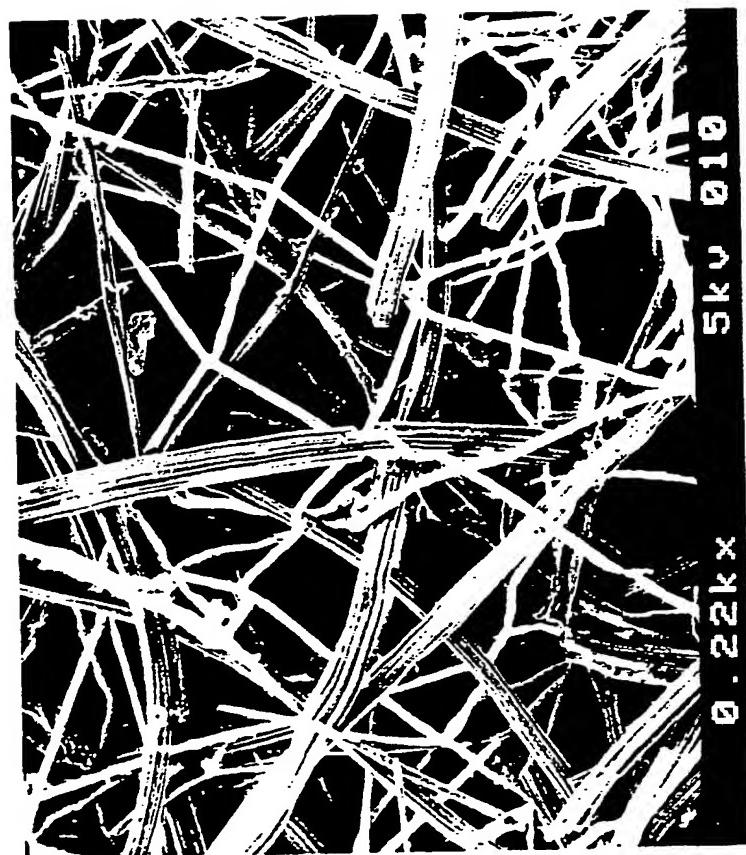
FIG.5
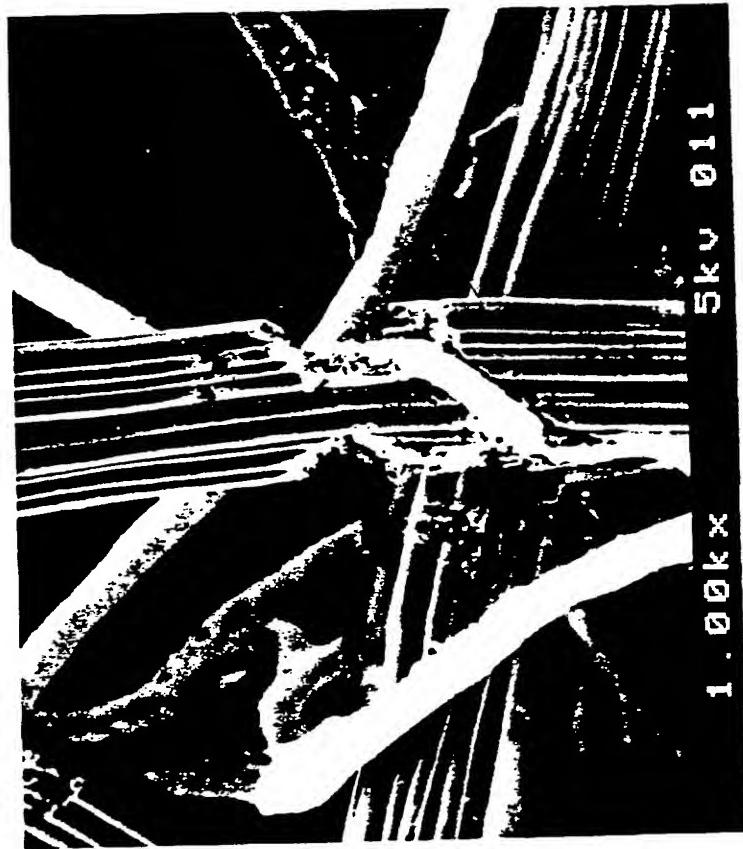
FIG.6
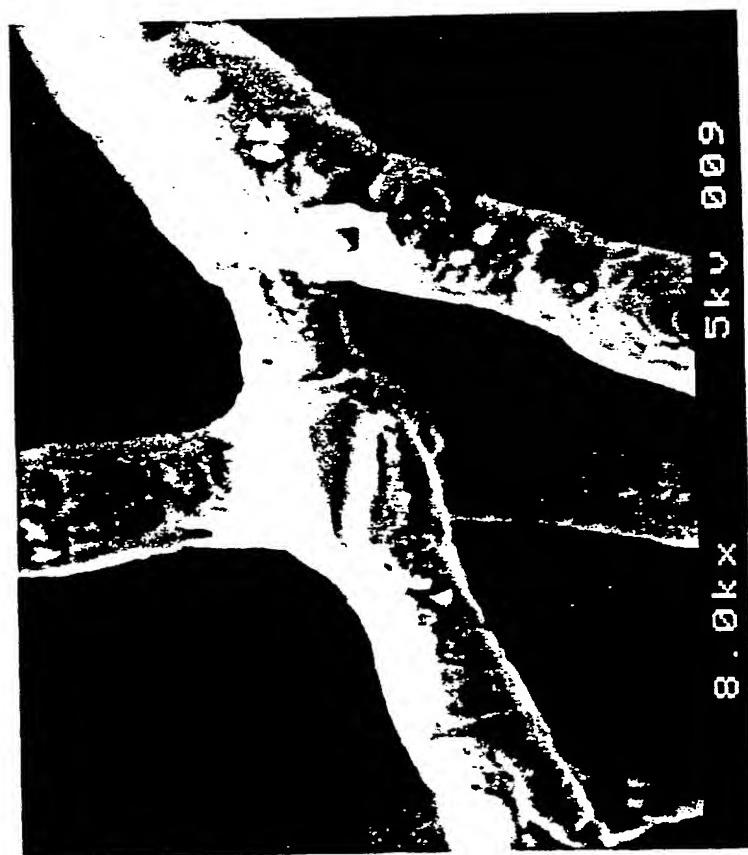
FIG.7
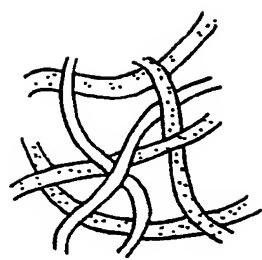
FIG.8A

FIG.8D

FIG.8C

FIG.8B

FIG.9

FIG.IO
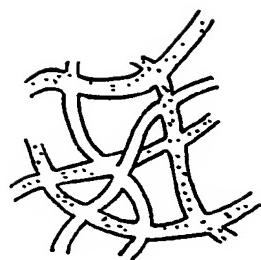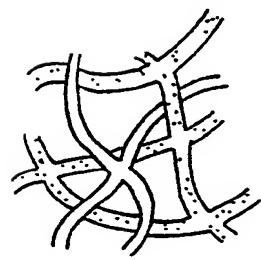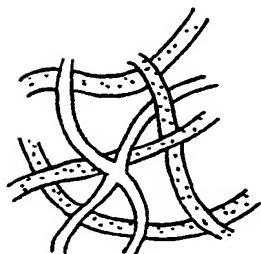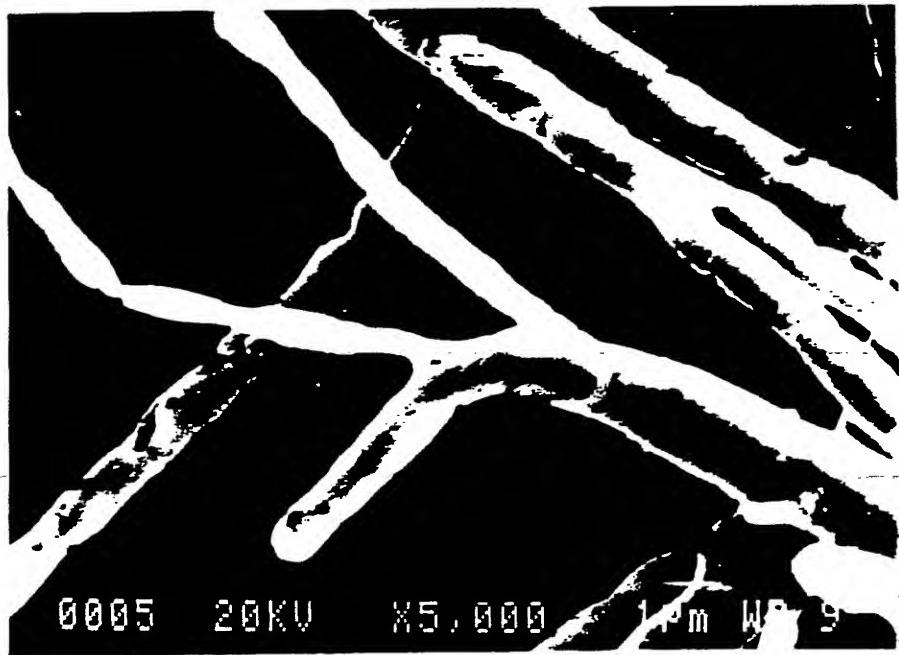
FIG.1

FIG.12

11/14

FIG.13

FIG.14
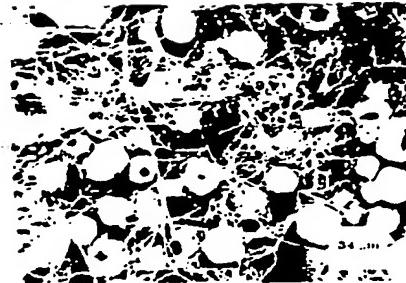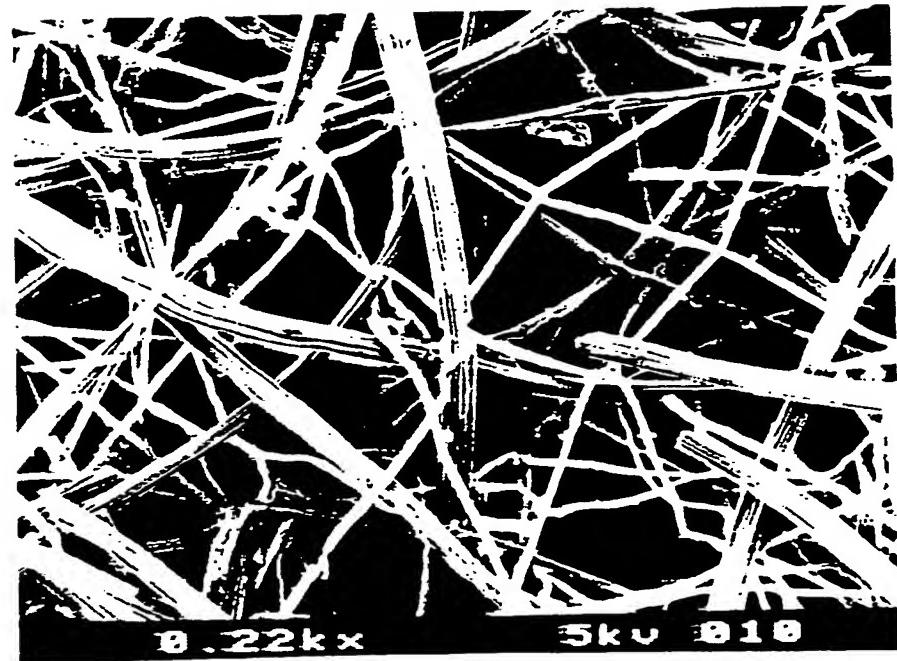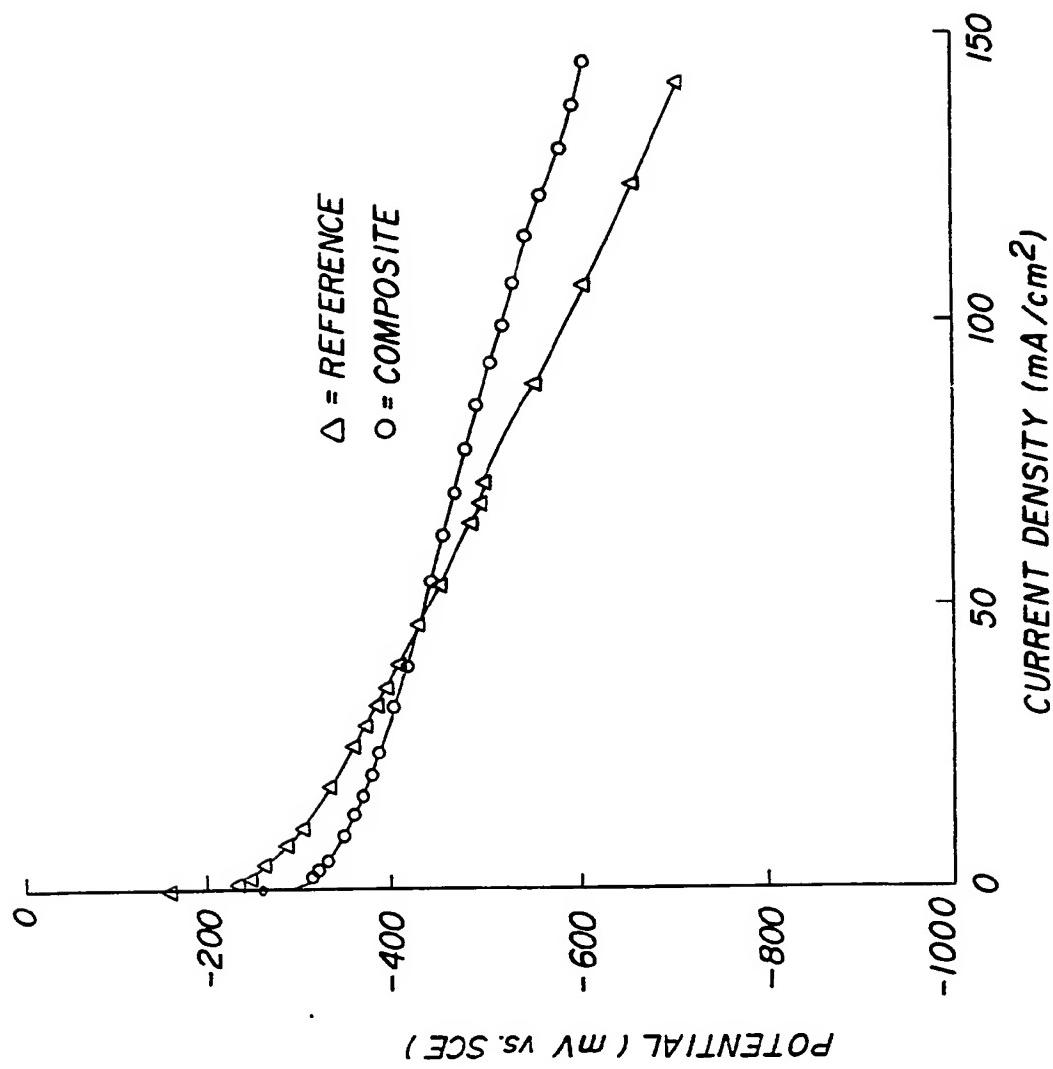
FIG.15

FIG.16

FIG.17

FIG.18

$\triangle$ = REFERENCE
O = COMPOSITE

CURRENT DENSITY (mA/cm^2)

POTENTIAL (mV vs. SCE)

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 3

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): B32B 15/14 B32B 5/08
US. CL.: 428/225,539.5, 605, 608; 204/242;264/60; 427/121

II. FIELDS SEARCHED

Minimum Documentation Searched 4

Classification System	Classification Symbols
U.S.	428/225,293, 457, 539.5, 545, 605, 607, 608 204/11, 12, 27, 28,242, 252, 254, 282, 290R, 294 427/121; 264/60, 61, 63

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 5

III. DOCUMENTS CONSIDERED TO BE RELEVANT 14

Category *	Citation of Document, 16 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 18
Y	US, A, 1,934,643 (RAFTON) 07 November 1933 Note page 3, column 1, lines 37-53.	1,2,6-13
Y	US, A, 2,616,165 (BRENNAN) 04 November 1952 Note column 1, lines 11-35.	1-5, 12-16
Y	US, A, 3,127,668 (TROY) 07 April 1964 Note column 3, lines 43-53 and column 4, lines 29-40	1, 2, 6-11, 33, 57-88
Y	US, A, 3,161,478 (HESSIN) 15 December 1964 Note column 2, lines 47-60; column 3, lines 25-47.	1, 2,6-13
Y	US, A, 3,310,387 (SUMP) 21 March 1967 Note column 4, lines 22-55; column 7, lines 39-54.	1, 2, 6-11
A	US, A, 3,694,325 (KATZ) 26 September 1972 Note column 6, lines 46 - column 7, line 7.	1-88
A	US, A, 3,905,831 (BROWN) 16 September 1975 Note column 6, lines 32-49.	1-88
A	US, A, 4,435,252 (KADIJA) 06 March 1984 column 2, lines 29-41; column 3, lines 13-68.	1-56

* Special categories of cited documents: 15

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 2	Date of Mailing of this International Search Report 2
06 AUGUST 1990	18 SEP 1990
International Searching Authority 1	Signature of Authorized Officer 20
ISA/US	JOHN J. ZIMMERMAN

Form PCT/ISA/210 (second sheet) (May 1986)

III. DOCUMENTS CONSIDERED TO BE RELEVANT   (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
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Y	US, A, 4,471,015 (EBNETH) 11 September 1984 Note column 2, lines 54-60.	1-56
Y	US, A, 4,597,028 (YOSHIDA) 24 June 1986 Note column 11, lines 5-63.	1-56
A	US, A, 4,643,940 (SHAW) 17 February 1987 Note column 3, lines 20-45.	1-88
Y	US, A, 4,737,889 (NISHINO) 12 April 1988 Note column 4, lines 11-40.	35-48
A	US, A, 4,743,349 (BACHOT) 10 May 1988 Note column 1, lines 58-column 2, lines 19; column 2, lines 45-58.	1-88
Y P	US,A , 4,874,677 (REICHE) 17 October 1989 Note column 2, lines 59-column 3, line 12.	1, 2, 6-13
Y	US, A, 4,882,227 (IWASE) 21 November 1987 Note column 5, lines 50-57; column 6, lines 22-44.	20-56
Y	GB, A, 821,690 (ARMOUR) 14 October 1959 Note page 2, lines 67-86, 105-128.	1, 2, 6-11, 57-88
A	GB, A, 942,513 (FRAM) 20 November 1963 Note page a, lines 34-43.	1-88
Y	EP, A, 74,263 (McCLENAHAN) 16 March 1983 Note pages 3 and 4.	20-56
A	METAL PROGRESS, March 1955, A. G. Metcalfe, "Fiber Metallurgy page 81-84	1-88
Y	THE IRON AGE, 24 January 1963, C. L. Kobrin, "Fiber Metals: A New adventure in Engineering Materials", pages 53-55.	1, 2, 6-11, 57-88

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